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Notice to Contributors

A RECORDING SYSTEM DESIGNED FOR THE INVESTIGATION OF THE ELECTRICAL RELATIONS IN THE BRAINS OF SMALL ANIMALS[1]

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Abstract

A two channel recording system, designed for the investigation of brain potential variations in several parts of the brain simultaneously, is described in detail. The oscillographs are of the cathode-ray type; each is driven by a voltage amplifier employing standard radio tubes. Complete shielding of the amplifier components and the use of symmetrical circuits have been found sufficient to eliminate electrical interference.

The system is free from phase and frequency distortion between 10 and 800 cycles per sec. and is not seriously affected by either form of distortion between 5 and 1500 cycles per sec. The author believes that this covers the important frequency range for this type of investigation.

Introduction

The investigation of the minute, transient electromotive forces generated in the brain of man and of the lower animals has become an important branch of medical research. This paper describes physical equipment designed especially for quantitative recording of such potential variations. The equipment has been in service for more than two years and has been applied to the investigation of the electrical relations in the cerebral cortex of cats and rabbits.

Four oscillograms typical of those recorded from the cerebral cortices of cats and rabbits are reproduced in Fig. 1. Records from the exposed cortex of the narcotized animal invariably exhibit a transient wave form (1-A and 1-B), except that under certain special experimental conditions (1-C) a semi-periodic wave form may appear. The amplitude and period of the electrical impulses from the normal cortex show a qualitative relation such that impulses of large amplitude usually have a long period; this relation often disappears under experimental conditions. The periods of the impulses have been observed to lie between 0.75 and 0.01 sec. and their amplitudes between 10 and 500 μv.
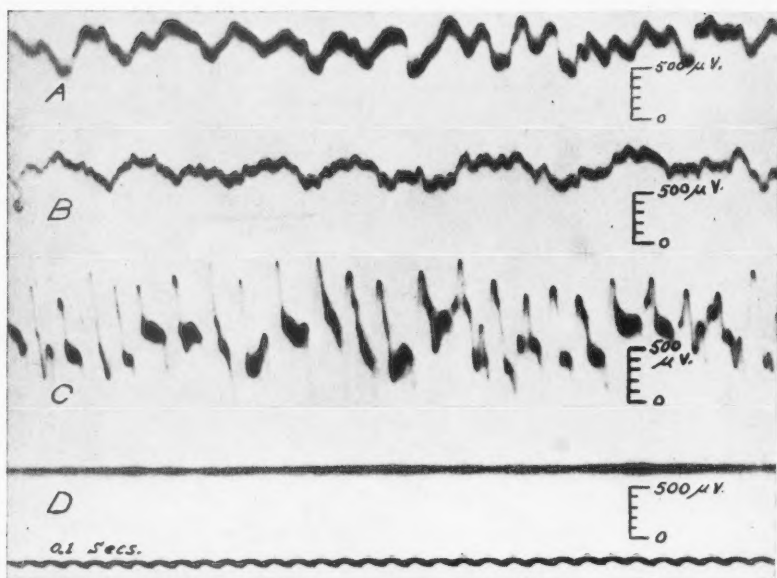
FIG. 1.   *A – C, oscillograms of action potentials developed in exposed cortex of anaesthetized rabbit; D, control from brain of same rabbit killed with chloroform.*

The Recording System—Amplifier

The recording system consists of two identical recording channels so arranged that simultaneous records from several parts of the brain may be photographed side by side on a strip of sensitive paper.   Each channel consists of a high gain voltage amplifier and a cathode-ray oscillograph.   An optical system collects the light from the two cathode-ray tubes and projects the two beams through the slit of a standard moving paper camera.   A supplementary mechanical oscillograph carrying a current of known frequency projects a third beam, which registers a time axis on the record.

Fig. 2 is the circuit diagram of one of the amplifiers.   It is divided into a pre-amplifier stage, which is located close to the animal, and the main amplifier, which is mounted on a rack beside the recording bench. The input and output stages of the amplifier are of push-pull design for special reasons; the two intermediate stages are also push-pull in order to maintain the symmetry of the system without the introduction of troublesome phase-splitting stages.   The circuit deviates from standard design only in the very great time constants of the coupling networks, which permit the response of the amplifier to be extended to frequencies below one cycle per second.   Because of the degenerative effect of any practical reactive element at these low frequencies, no attempt has been made to introduce automatic biasing or to use common grid and plate batteries.   Separate flash-light cells have been used as bias batteries in

INPUT STAGE

FIG. 2. *Circuit diagram of one of the amplifiers. All grounds are made at one common point. The copper electrostatic shield, which forms the conduit for the leads between main and pre-amplifier, also serves to connect the pre-amplifier's electromagnetic shields to ground.*

xx — *input leads*	c,g,c, — *leads to the cathode-ray oscillograph*
R_1 — *50,000 ohms, wire wound*	E_1 — *1.5 v., flash-light cell*
R_2 — *200,000 ohms, wire wound*	E_2 — *6 v., dry cells*
R_3 — *2 megohms*	E_3 — *180 v.*
R_4 — *50,000 ohms, precision, carbon*	E_4 — *6 v., miniature "C"*
R_5 — *2 megohms total, tapped*	E_5 — *225 v.*
R_6 — *100,000 ohms, precision, carbon*	E_6 — *270 v.*
R_7 — *25,000 ohms, precision, carbon*	NOTE—*The main amplifier filaments*
R_8 — *500,000 ohms, precision, carbon*	*are heated by a common, 6 v. battery.*
C_1 — *2 µf.*	T_1 — *6F5G*
C_2 — *4 µf.*	T_2 — *76*

each stage and three sets of plate batteries have been found necessary for the four stages.

Matthews (2) has shown that amplifiers employing a single tube in the input circuit interact with one another when connected to neighbouring parts of the brain, and he has used push-pull input circuits to avoid this effect.   The input circuit of this amplifier is a modification of that of Matthews, differing mainly in the omission of a ground connection.   No instabilities due to this

modification have ever been observed and, at least theoretically, greater freedom from interaction is obtained.   Tests have shown that the two amplifiers operate independently when the electrodes are within a few millimetres of one another on the surface of the brain.   Even when one amplifier is used alone this type of circuit should be employed.   Parts of the animal, leads, and all other components not grounded directly or through a low resistance are usually at some alternating potential relative to ground because of low frequency, lighting-circuit fields.   This potential difference is amplified by a single tube input circuit in which the cathode of the tube is near ground potential but is rejected by a push-pull circuit since the alternations are in phase at the two grids.

The push-pull output circuit permits peak potential differences of the order of 100 v. to be applied to the deflecting plates of the cathode-ray oscillograph without amplitude distortion; these large voltages are made necessary by the small voltage sensitivity of this type of oscillograph.

Special low-noise tubes were found to be unnecessary in the input circuit of the amplifier for the present application but would probably be required if operation at higher sensitivities, such as that required for records from single nerve fibres, were attempted.   An approximate measurement of combined shot, flicker, and thermal agitation voltages in the 6F5G input tubes gave an equivalent input noise, integrated over the whole pass band of the amplifier of about 6 r.m.s. μv.   The thermal agitation noise contributed by the external grid circuit and grid resistors is negligibly small since the equivalent resistance of the input circuit falls to a few thousand ohms when connected to the cortex of the animal.   Noises due to discontinuous conduction in composition resistors have been avoided by the use of wire wound resistors in the grid and plate circuit of the first stage.   The rigid cathode structure of the 6F5G tube makes it much less microphonic than those tubes in which a tungsten filament is used to minimize flicker voltage.

The same type of tube, 6F5G, has been found to be satisfactory in all but the output stage of the amplifier.   Because of its large amplification factor comparatively few stages are required; the large effective input admittance, which is necessarily associated with the large amplification factor, is not a serious defect since in this application the amplifier is not required to respond to frequencies above a few thousand cycles per second.   The average grid current for the tube is about 10^{-8} amp. so that it may be used in circuits of very great time constant without appreciable loss of bias.

The electromagnetic, mechanical, and acoustical shielding of the amplifier was designed to eliminate the effect of low frequency (25 cycles per sec.) electromagnetic fields, building vibrations, and acoustical shocks, and at the same time to permit easy access to the amplifier components.   Each stage was built on a shelved, cylindrical, bakelite rack (Fig. 3) on which were mounted tubes, bias battery, grid resistors, and coupling condensers for the stage and the plate resistors for the preceding stage.   The two bottom bakelite sections of the rack were mechanically isolated by means of a thick pad of
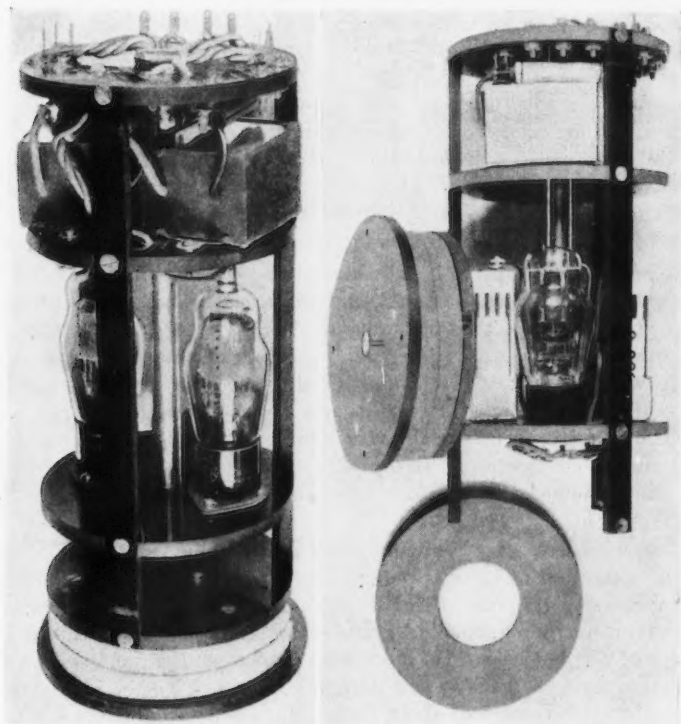
FIG. 3.   *The internal construction of the amplifier stages.   The components of each stage are mounted on a bakelite rack, the whole being supported by a sponge rubber pad.*

sponge rubber in order that the inertia of the rack and amplifier components could be used to minimize vibration.   The mechanical insulation of the rack was maintained by the use of fine wires for connection between terminals on the top of the rack and terminal strips on the inside wall of the metal shields. In addition to these precautions, the tubes of the pre-amplifier were wrapped in felt and lead acoustical shields and mounted loosely in cotton; connections to the tubes were made through fine flexible wires soldered to their bases. Separate cylindrical, electromagnetic shields, just large enough to hold the bakelite racks, were used for each stage, and other shields of appropriate shape were used to house the various banks of batteries.   At the lighting-circuit frequency (25 cycles per sec.), electromagnetic shielding by eddy currents in simple electrical conductors was found to be very inefficient, and the type of laminated shielding suggested by Metcalf and Dickinson (3) was adopted. In this case the shields consist of three layers of silicon-steel sheet separated by and interleaved with two layers of copper; the effectiveness of the shield is due to the large counter magnetomotive force generated by the eddy cur-

rents which are induced in the layers of copper by the magnetic induction in the adjacent layers of high permeability steel. Fewer laminations would be satisfactory for shielding from fields of 60 cycles per sec.

Leads between the amplifier and pre-amplifier, between batteries and amplifiers, and between the animal compartment and the pre-amplifier, were electrostatically shielded by means of copper conduits. A large, grounded, iron box, fitted with a door which opened along one side was found to shield the animal adequately; the simplicity of the shield for the animal is made possible by the push-pull input circuit.

The blank control of Fig. 1-D, recorded at the same sensitivity as 1-A, etc., but after the animal was killed with chloroform, is an indication of the sufficiency of the shielding. The necessity of the various precautions was determined during construction. For example, the same amplifier operated at the same sensitivity but without mechanical or acoustical shielding was found to respond to the building vibration caused by a 1 lb. weight dropped 3 ft. to the floor in a room 75 ft. from that in which the amplifier was located; the present amplifier is insensitive to ordinary building vibrations but vibrational effects can be induced by a smart blow on the floor near the pre-amplifier location.

The amplification factor of the amplifier is 1.4×10^5 for normal operation in the investigation of cortical potentials. At this amplification and up to double this value no trace of input noise or microphonics appears in the record. The maximum amplification factor has been measured and found to be 1.4×10^6, but because of input disturbances and microphonics a maximum usable limit has been set at an amplification of 5.6×10^5 times. At this value a noise voltage of about four volts is generated across the output terminals, and voltages of about the same value due to microphonics are superimposed at random.

Oscillographs, Optical System, and Camera

The recording system employs two R.C.A. high-vacuum cathode-ray tubes, Type 907. Besides exhibiting a constant sensitivity over the whole important frequency spectrum, the cathode-ray oscillograph has a decided advantage over other types when low frequency impulses are to be recorded. The tube with stabilizing network has a purely resistive input impedance of several megohms, so that it may be driven by a voltage amplifier and coupled to it by networks of the same type and characteristics as those used between stages. High-vacuum tubes were chosen in order to avoid troublesome corrections for threshold errors which are common to gas tubes, and because the "grid" or control electrode of a high-vacuum tube permits control of brilliance independent of focus or sensitivity. A voltmeter shunted across the control electrode circuit is used in this recording system as an indirect but effective brilliance meter by which exposures can be duplicated from day to day. The oscillograph tubes are mounted in laminated shields to minimize the effect of stray fields, and also to shield out an abnormally large vertical mag-

netic field component probably associated with the metal girders used in the construction of the building in which this equipment is housed.

The two oscillographs and a motor-driven Stoppani camera were so set up that the tubes faced each other with their long axes parallel to the camera slit. Two optical systems, one for each tube, each consisting of a mirror set at 45° to the screen of the tube and a 6.5 diopter achromatic doublet of 5 cm. aperture, serve to reflect the light from the fluorescent spot through 90°, collect it, and bring it to focus, without magnification in the plane of the sensitive paper in the camera.

The maximum spot velocity which has been observed in recording cortical potentials with this apparatus is 70 cm. per sec. In order to produce satisfactory records, fluorescent screen, optical system, and emulsion must be so chosen that tracings of adequate density are produced at the highest spot velocity, but at a spot intensity which is matched to the latitude of the paper in such a way that the tracing is readable at spot velocities near zero. The combination of the phosphor No. 5 screen of the Type 907 oscillograph, when operated at an anode No. 2 voltage of 1500 volts, and Ilford F.P. 1 oscillograph paper has produced satisfactory records with this optical system at maximum spot velocities up to 100 cm. per sec.

Time and Voltage Axes

The timing oscillograph consists of a light spindle carrying a small iron armature and a mirror that oscillates in the crossed fields of two pairs of electromagnets. One pair of the electromagnets carries a direct current; the action of its field on the armature constitutes the restoring couple of the oscillating system. The vibromotive force is supplied by the other pair of coils through which flow the alternating, timing current. A substantially sinusoidal timing wave of current is obtained by passing the square current wave from a Palmer one-tenth second vibrator through a low pass filter; the sinusoidal wave form has been found necessary because of interference produced by the upper harmonics of the square wave.

At the end of each experiment a short record of a 25 cycles per sec. wave, produced by a known alternating voltage applied to the input of the system, is photographed. The amplitude of the applied voltage and of the recorded wave provides sufficient information for the calculation of the sensitivity of the system. The amplitude of the applied voltage is determined by a peak voltmeter, of the type described by Ruiz (4), modified to use a Type 885 grid glow tube. Voltage measurements are made across the outside of a symmetrical potential divider circuit, the centre of which is grounded. The voltage to be applied to the recording system is picked off on each side of ground, near the centre of the network.

Electrodes

A variety of electrodes for making contact with the cortex of the brain have been tried. Because of the large input impedance of the amplifier, the internal resistance of the electrodes can have values up to several thousand ohms without affecting results; such resistance requirements can be met by almost any type of material when soaked in saline of physiological concentration. Direct contact with the cortex through silver wires coated with silver chloride has been found to pick up pulsations of the brain. Fine, flexible, camel's-hair brushes, thoroughly soaked in Ringer-Locke solution, have proved most satisfactory; the brushes are made by binding tufts of hair, about 2 cm. long to chlorided silver wires. Coarser electrodes made by binding absorbent cotton to silver wires have been found useful when less exact localization of contact is permissible.

Sensitivity and Over-all Response of the System

The sensitivity of the system has been measured at constant frequency for a wide range of input voltages and has been found constant for all input voltages that produce a peak deflection of the fluorescent spot of less than 3 cm. It is concluded, from these measurements, that the records are free from amplitude distortion provided that they are not allowed to exceed the limiting amplitude; at the limiting amplitude the peak output voltage from the amplifier is 120 v.

The relation between frequency and the over-all sensitivity of the system was found by measurement with the help of a specially designed low frequency beat frequency oscillator, and the relation between phase and frequency was calculated from this measurement and from the known constants of the coupling networks. Both relations have been given graphical expression in Fig. 4. The system is free from both kinds of distortion between 10 and 800 cycles per sec. and is not seriously affected by either form between 5 and 1500 cycles per sec. Since 1500 cycles corresponds to the fifteenth harmonic of the fastest impulse ever observed, it is believed that the upper frequency parts of the response curves are entirely satisfactory in the present application. Phase and frequency distortions undoubtedly appear because of the inability of reactively coupled amplifiers to respond at zero frequency, but Adrian and Matthews (1) have controlled this source of error in the recording of cortical potentials by simultaneous recording with a resistance-capacity and a galvanically coupled amplifier. They found no differences likely to affect interpretation and note that there was very little difference of any kind in the two records. A further investigation of this point is planned.

The curvature of both phase and sensitivity characteristics at low frequency is an expression of the time-constants and of the number of coupling networks employed in the system; the over-all phase angle is more directly affected by the number of stages than is the sensitivity, because phase shifts add from stage to stage.
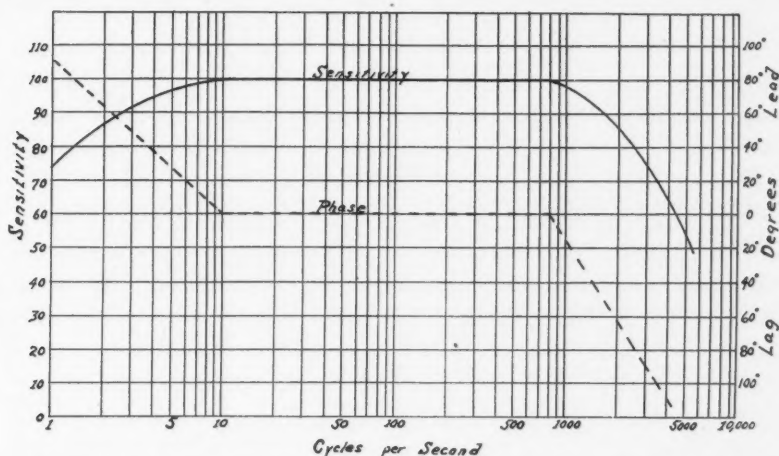
FIG. 4.   *Over-all sensitivity and phase of the recording system as a function of frequency.*

The falling sensitivity and lagging phase characteristics at high frequency are due in part to stray reactive circuits to the shields but mainly to the high equivalent input admittance of the high gain tubes that are used.   An extended high frequency response is not compatible with an extended low frequency response because the first requires more stages employing tubes with lower amplification factors, while the second requires the opposite.   Because of the transient and low frequency nature of the cortical impulses, the low frequency response of this system was emphasized at the expense of the high.

The system is usually operated at a sensitivity of 2 to 3 cm. per mv. (measured on the flat part of the sensitivity-frequency curve) for adequate records from the cortices of small animals, but can be operated at a sensitivity of 7 cm. per mv. without extraneous interference.   The theoretical upper limit of sensitivity is 35 cm. per mv., but the relative amplitude of the input disturbances render the record quite unreadable at sensitivities higher than 14 cm. per mv.

Acknowledgments

References

1. ADRIAN, E. D. and MATTHEWS, B. H. C.   J. Physiol. 81 : 440-471.   1934.
2. MATTHEWS, B. H. C.   J. Physiol. 81 : 28P-29P.   1934.
3. METCALF, G. F. and DICKINSON, T. M.   Physics, 3 : 11-17.   1932.
4. RUIZ, J. J.   Rev. Sci. Instruments, 6 : 169-171.   1935.

TAIL BANDS OF THE DESLANDRES-D'AZAMBUJA SYSTEM OF THE C_2 MOLECULE[1]

By G. Herzberg[2] and R. B. Sutton[3]

Abstract

A number of new bands of the C_2 molecule are analysed and found to represent tail bands of the Deslandres-d'Azambuja system. In consequence of the extension of this system thus obtained it was possible to improve considerably on the values of the rotational and vibrational constants of the upper and lower states $^1\Pi_g$ and $^1\Pi_u$ respectively. The vibrational quanta of the upper state are found to decrease rather rapidly, and a short extrapolation leads to a dissociation limit at 35,900 cm.$^{-1}$ above the lower state $^1\Pi_u$. From this and a recently suggested $D_0(C_2)$ value, the energy difference between the $^1\Pi_u$ state and the $^3\Pi_u$ ground state is determined to be 13,700 cm.$^{-1}$ = 1.7 e.v.

Introduction

In order to obtain a reliable value for the heat of dissociation $D_0(C_2)$ of the C_2 molecule, the authors have continued the re-investigation of the spectrum of C_2 started two years ago by Fox and Herzberg (2). While it has not yet been possible to obtain a satisfactory solution of the original problem, it has been possible to analyse a number of the C_2 bands left unexplained by Fox and Herzberg. These bands form an interesting extension of the Deslandres-d'Azambuja system analysed by Dieke and Lochte-Holtgreven (1) and Kopfermann and Schweitzer (6), and they advance considerably our knowledge of the two electronic states involved.

Experimental

The C_2 bands were excited in an uncondensed discharge through an ordinary II-shaped tube filled with helium of about 1 cm. pressure into which pure benzene was slowly admitted. Under these conditions the C_2 and CH bands appeared with great intensity. Only the strongest sequence of CN, at 3883 Å, and the NH band at 3300 Å were noticeable as impurities. They did not, however, interfere with the measurement of the C_2 bands.

The spectra were photographed in the second order of the new 20-ft. grating spectrograph of this department. The grating, ruled by R. W. Wood, has an exceptional brightness in the second order for 3000 to 4000 Å, and, consequently, the exposure times were only from 5 to 45 min. The dispersion is 1.3 Å per mm. in the second order. The spectrograms were measured under a Gaertner comparator.

Analysis of the Vibrational Structure

Two of the unclassified bands found by Fox and Herzberg lie on the long wave-length side of the sequence $\Delta v = 2$ of the Deslandres-d'Azambuja system. Two other such bands lie on the long wave-length side of the sequence $\Delta v = 1$. Three of these bands are shaded to the red, that is, oppositely to the Deslandres-d'Azambuja bands thus far known. But an inspection of their fine structure under high dispersion shows that they have otherwise the same structure as the former bands. This suggested that they are "tail" bands of the Deslandres system, that is, bands with higher v values on the returning limb of the parabolas representing the corresponding sequences [see Herzberg (4)]. This assumption will indeed be shown to be valid by the more detailed analysis of both the vibrational and rotational structure.

Table I gives the wave-lengths of the heads and the wave numbers of the zero lines of all the bands measured by Dieke and Lochte-Holtgreven and by the authors. The zero lines ν_0 of the bands whose fine structures were analysed (see below) were obtained from the first fifteen $R(J - 1) + P(J)$ values in the manner described by Herzberg (4). Also the zero lines of the bands analysed by Dieke and Lochte-Holtgreven were recalculated in this way; this led to slight changes of their ν_0 values. In addition to the four new bands mentioned above, the fine structure of the 3–1 band, the second band of the sequence $\Delta v = 2$ has also been analysed. The figures in parentheses in Table I refer to bands whose fine structure has not been analysed.

TABLE I

SCHEME OF BAND HEADS AND OF BAND ORIGINS OF THE DESLANDRES-D'AZAMBUJA SYSTEM OF C₂

v' \ v''	0	1	2	3	4	5
0	3852.1V 25969.22	4102.3V 24385.10				
1	3607.3V 27733.57	3825.6V 26149.53	4062.2V 24589.78			
2	3399.8V (29430.3)	3592.9V 27846.12		4041.9V 24750.68		
3		3398.1V 29450.74	3587.6V (27891.1)		4026.9V* (24844.7)	
4			** V 29359.22	3599.3V† (27816.5)		
5				3431.9R 29082.56	3617.9R 27571.41	
6						3689.0R 27081.33

V means shaded to the violet, R means shaded to the red.
* This band has only been measured by Johnson (5).
** This band has no head.
† This head is not very well defined.
The bands with $v' = 4, 5, 6$ have not been given before.

Their zero lines have been obtained from the measured band heads using the B_v values known from the other bands.

Table II gives the vibrational quanta ΔG for the upper and lower electronic states of the bands as obtained from the data of Table I. The vibrational quanta of the lower state $\Delta G''$ decrease very nearly linearly with v, whereas those of the upper state, $\Delta G'$, decrease much more rapidly. However, they also fall on a smooth curve, thus confirming that the new bands belong to the Deslandres-d'Azambuja system. The lower state vibrational levels can be very well represented by

$$G''(v'') \;=\; 1608.34 \,(v'' + \tfrac{1}{2}) \;-\; 12.14 \,(v'' + \tfrac{1}{2})^2$$

There is, however, not much point in giving a formula for the upper state, since as many terms as there are quanta would be needed. Instead, Table III gives the position of the upper vibrational levels above the $v'' = 0$ level of the lower state*.

A short extrapolation of the vibrational levels of the upper state yields for the dissociation limit 35,900 cm.$^{-1}$ above the level $v'' = 0$. It is not possible to draw any conclusions from this concerning the dissociation energy D_0 of C_2,

TABLE II

VIBRATIONAL QUANTA IN THE UPPER AND LOWER STATES OF THE
DESLANDRES-D'AZAMBUJA BANDS

v	$\Delta G''_{v+\frac{1}{2}} =$ $G''(v+1) - G''(v)$	$\Delta^2 G''$	$\Delta G'_{v+\frac{1}{2}} =$ $G'(v+1) - G'(v)$	$\Delta^2 G'$
0	1584.08		1764.39	
		24.33		67.80
1	1559.75		1696.59	
		24.06		91.97
2	1535.69		1604.62	
		24.54		136.39
3	1511.15		1468.23	
				209.20
4			1259.03	
				262.17
5			(996.86)	

The $\Delta G'$ value in parentheses has been obtained by using an extrapolated value for $\Delta G''_{4\frac{1}{2}}$.

TABLE III

ENERGIES OF THE UPPER VIBRATIONAL LEVELS ABOVE $v'' = 0$

v'	$T_0 + G'(v)$, cm.$^{-1}$	v'	$T_0 + G'(v)$, cm.$^{-1}$
0	25969.19	4	32503.06
1	27733.59	5	33761.94
2	29430.10	6	34758.83
3	31034.80		

* The $\Delta G'$ values obtained from Table III do not exactly coincide with those of Table II, since the $T_0 + G'$ values of Table III were obtained by averaging over all bands with equal v'.

since the height of the lower state of the Deslandres-d'Azambuja system ($^1\Pi_u$) above the ground state $^3\Pi_u$ (lower state of the Swan bands) is not known. However, conversely, using the above dissociation limit this height may be determined approximately, if a tentative value $D_0(C_2) = 3.6$ e.v. $= 29,200$ cm.$^{-1}$, recently suggested by Herzberg (3) is assumed to be correct. The energy difference in question is then $29,200 + A - 35,900 = A - 6700$ cm.$^{-1}$, where A is the excitation energy of the products of dissociation at the dissociation limit of the upper state ($^1\Pi_g$) of the Deslandres-d'Azambuja system. $A = 0$ would correspond to a dissociation of $^1\Pi_g$ into normal atoms $^3P + {}^3P$. This appears to be impossible since it would put the $^1\Pi_u$ state lower than the $^3\Pi_u$ state, which is generally considered to be the ground state of C_2. The next possibility for the dissociation products is $^1D + {}^1D$ (since $^3P + {}^1D$ does not lead to a $^1\Pi_g$ state) leading to a value of $A = 20,400$ cm.$^{-1}$, and thus to 13,700 cm.$^{-1}$ $= 1.7$ e.v. for the energy difference of $^1\Pi_u$ and $^3\Pi_u$. Any other assumption about the dissociation products of $^1\Pi_g$ would lead to a much larger difference in energy, which seems to be ruled out because $^1\Pi_u$ and $^3\Pi_u$ have the same electron configuration. Also the value 1.7 e.v. is in fair agreement with a theoretical estimate of 2.1 e.v. given by Mulliken (7).

Analysis of the Rotational Structure

The Deslandres-d'Azambuja bands are known to represent a $^1\Pi_g - {}^1\Pi_u$ transition. Each band consists therefore of three branches, P, Q, and R, of which the Q branch is very weak. For heteronuclear molecules, in a $^1\Pi - {}^1\Pi$ transition, every line splits into two components in consequence of Λ-type doubling, but for homonuclear molecules with zero nuclear spin, such as C_2, alternately the long and the short wave-length components of the Λ-doublets are missing, and a "staggering" of the lines in a branch (instead of a doubling) results. This staggering is very clearly observed in the new as well as the old bands of the Deslandres-d'Azambuja system.

In Table IV the wave numbers of the lines in the P and R branches of the five bands that have been analysed are given. The Q branches that were observed for some of the bands are not given because they consist only of very few lines. Table V shows the combination differences $\Delta_2 F'(J) = R(J) - P(J)$ and Table VI the combination differences $\Delta_2 F''(J) = R(J-1) - P(J+1)$. It is seen that the $\Delta_2 F'$ values for the 5–3 and 5–4 bands agree in a very satisfactory way. Similarly the $\Delta_2 F''$ values for the 3–1, 4–2, and 5–3 bands agree with those given by Dieke and Lochte-Holtgreven for the 0–1 (and 1–1, 2–1), 1–2, and 2–3 bands respectively. This agreement confirms again that the new bands belong to the Deslandres-d'Azambuja system.

The rotational constants B_v and D_v were evaluated from the $\Delta_2 F$ values in the usual manner [see Herzberg (4)]. In this calculation the $\Delta_2 F$ for even and odd J were not treated separately, since the "staggering" of the $\Delta_2 F$ values was usually slight. Thus the B_v and D_v values obtained are average B_v and D_v values for the two Λ-components. Wherever possible the averages of corresponding $\Delta_2 F$ values of different bands with the same upper or the

TABLE IV

WAVE NUMBERS OF THE LINES IN THE NEW BANDS OF THE DESLANDRES-D'AZAMBUJA
SYSTEM

J	3 – 1 Band $\nu_0 = 29,450.74$		4 – 2 Band $\nu_0 = 29,359.22$		5 – 3 Band $\nu_0 = 29,082.56$	
	$R(J)$	$P(J)$	$R(J)$	$P(J)$	$R(J)$	$P(J)$
1	29,457.68		29,365.77		29,088.59	
2	61.46	29,444.34	69.20	29,353.00	91.45	29,076.33
3	65.27	41.77	72.71	50.09	94.35	73.02
4	69.23	39.08	76.22	47.17	97.06	69.67
5	73.50	36.61	79.91	44.37	99.80	66.36
6	77.82	34.31	83.64	41.61	102.34	
7	82.44	32.12	87.52	39.04	04.83	59.32
8	87.07	30.05	91.31	36.43	07.40	55.62
9	92.03	28.40	95.42	34.02	09.80	51.97
10	96.83	26.67	99.31	31.54	11.88	48.30
11	502.37	25.27	403.61	29.34	14.20	44.50
12	07.56	23.84	07.50	26.98	16.06	40.40
13	13.26	22.87	12.01	24.96	18.22	36.52
14	18.74	21.77	16.07	22.71	19.80	32.17
15	24.88	20.71	20.71	20.94	21.78	28.17
16	30.57	20.25	24.75	18.68	23.09	23.54
17	37.05	19.74	29.61	17.03	24.84	19.37
18	42.99	19.39	33.79	14.94	25.74	14.42
19	49.89	19.39	38.80	13.53	27.32	10.03
20	56.09	19.39	42.88	11.40	27.87	04.78
21	63.66	19.74	47.96	10.14	29.21	00.20
22	69.61	20.25	52.14	08.07	29.21	28,994.57
23	77.00	21.18	56.76	06.87		89.73
24			61.46	04.89		83.70
25			67.13	03.28		78.54
26			70.80	01.81		72.06
27			76.37	01.29		66.53
28			80.47	298.77		59.54
29			86.05	98.13		53.89
30			89.50	96.12		46.04
31			95.18	95.40		40.20
32			98.41	92.80		31.84
33			504.03	92.33		25.61
34			07.56	89.54		16.13
35				89.03		09.93
36						899.05

TABLE IV—*Concluded*

WAVE NUMBERS OF THE LINES IN THE NEW BANDS OF THE DESLANDRES-D'AZAMBUJA
SYSTEM

J	5 – 4 Band $\nu_0 = 27,571.41$		6 – 5 Band $\nu_0 = 27,081.33$	
	$R(J)$	$P(J)$	$R(J)$	$P(J)$
1	27,577.45		27,086.74	
2	80.44	27,565.16	88.91	27,074.95
3	83.41	62.05	91.26	71.56
4	86.25	58.89	93.17	67.85
5	89.16	55.67	94.89	63.87
6	91.91	52.41	96.32	59.66
7	94.68	49.13	97.58	55.32
8	97.53	45.72	98.38	50.66
9	600.23	42.34	99.21	45.86
10	02.66	39.04	99.82	40.68
11	05.38	35.60	99.82	35.42
12	07.62	31.88	99.82	29.75
13	10.25	28.47	99.82	24.03
14	12.32	24.60	98.99	17.80
15	14.81	21.10	98.38	11.57
16	16.66	17.05	97.01	04.80
17	19.00	13.44	95.58	26,998.09
18	20.58	09.15	93.88	90.74
19	22.77	05.43	92.42	82.95
20	24.03	00.86	89.53	75.53
21	26.05	497.00	87.39	68.08
22	26.92	92.16	83.87	59.11
23	28.70	88.07	81.09	50.99
24	29.18	82.89	76.87	41.47
25	30.67	78.61	73.35	32.70
26	30.67	73.09	68.40	22.46
27	32.02	68.44	64.27	13.04
28	31.27	62.50	58.43	02.08
29	32.39	57.82	53.44	891.99
30	31.46	51.09	46.65	80.19
31	32.39	46.12	41.68	69.34
32		38.87	33.75	56.50
33			27.99	45.62
34			19.51	31.81
35			13.48	19.44
36			03.77	04.81
37			26,997.06	791.64
38			86.90	76.29
39				62.07
40				45.61
41				31.11
42				14.08

same lower state (including the $\Delta_2 F$ values given by Dieke and Lochte-Holtgreven) were used. Also the rotational constants for those vibrational levels for which only Dieke and Lochte-Holtgreven have data were recalculated according to the same procedure, in order to get as consistent a set of constants as possible. The results are given in Table VII.

TABLE V

COMBINATION DIFFERENCES FOR THE UPPER STATE $\Delta_2 F'(J) = R(J) - P(J)$

J	$v' = 3$	$v' = 4$	$v' = 5$		$v' = 6$
	(3–1)	(4–2)	(5–3)	(5–4)	(6–5)
2	17.12	16.20	15.12	15.28	13.96
3	23.50	22.62	21.33	21.36	19.70
4	30.15	29.05	27.39	27.36	25.32
5	36.89	35.54	33.44	33.49	31.02
6	43.51	42.03	39.53	39.50	36.66
7	50.32	48.48	45.51	45.55	42.26
8	57.02	54.88	51.78	51.81	47.72
9	63.63	61.40	57.83	57.89	53.35
10	70.16	67.77	63.58	63.62	59.14
11	77.10	74.27	69.70	69.78	64.40
12	83.72	80.52	75.66	75.74	70.10
13	90.39	87.05	81.70	81.78	75.79
14	96.97	93.36	87.63	87.72	81.19
15	103.17	99.77	93.61	93.71	86.81
16	110.32	106.07	99.55	99.61	92.21
17	117.31	112.58	105.47	105.56	97.49
18	123.60	118.85	111.32	111.43	103.14
19	130.50	125.27	117.29	117.34	109.47
20	136.70	131.48	123.09	123.17	114.00
21	143.92	137.82	129.01	129.05	119.31
22	149.36	144.07	134.64	134.76	124.76
23	155.82	149.89		140.63	130.10
24		156.57		146.29	135.40
25		163.85		152.06	140.65
26		168.99		157.58	145.94
27		175.08		163.58	151.23
28		181.70		168.77	156.35
29		187.92		174.57	161.79
30		193.38		180.37	166.44
31		199.78		186.27	172.34
32		205.61			177.25
33		211.70			182.37
34		218.02			187.70
35					194.04
36					198.96
37					205.42
38					210.61

Fig. 1 gives a graphical representation of the B_v curves. As can be seen from this figure, B_v'' is very closely a linear function of v'', whereas B_v' is not a linear function of v' but decreases much more rapidly. Thus, as usual, the behaviour of the B_v values is similar to that of the ΔG values.

The B_v'' values can be represented by

$$B_v'' = 1.6170 - 0.0172 \ (v'' + \tfrac{1}{2})$$

that is $B_e'' = 1.6170$ and $\alpha_e'' = 0.0172$ cm.$^{-1}$. A formula for the B_v' values would contain almost as many constants as there are B_v' values and is therefore not given here. An approximate value for B_e' obtained from the first three B_v' values is $B_e' = 1.7834$ cm.$^{-1}$. The values for the internuclear distances of the equilibrium position in the upper and lower states obtained

TABLE VI

COMBINATION DIFFERENCES FOR THE LOWER STATE $\Delta_2 F''(J) = R(J-1) - P(J+1)$

J	$v'' = 1$ (3–1)	$v'' = 2$ (4–2)	$v'' = 3$ (5–3)	$v'' = 4$ (5–4)	$v'' = 5$ (6–5)
2	15.91	15.68	15.57	15.40	15.18
3	22.38	22.03	21.78	21.55	21.06
4	28.66	28.34	27.99	27.74	27.39
5	34.92	34.61	34.25	33.84	33.51
6	41.38	40.87	40.48	40.03	39.57
7	47.77	47.21	46.72	46.19	45.66
8	54.04	53.50	52.86	52.34	51.72
9	60.40	59.77	59.10	58.49	57.70
10	66.76	66.08	65.30	64.63	63.79
11	72.99	72.33	71.48	70.78	70.07
12	79.50	78.65	77.68	76.91	75.79
13	85.79	84.79	83.89	83.02	82.02
14	92.55	91.07	90.05	89.15	88.25
15	98.49	97.39	96.26	95.27	94.19
16	105.14	103.68	102.41	101.37	100.29
17	111.18	109.81	108.67	107.51	106.27
18	117.66	116.08	114.81	113.57	112.63
19	123.60	122.39	120.96	119.72	118.35
20	130.15	128.66	127.12	125.77	124.34
21	135.84	134.81	133.30	131.87	130.42
22	142.48	141.09	139.48	137.98	136.40
23		147.26	145.51	144.03	142.40
24		153.48		150.09	148.39
25		159.65		156.09	154.41
26		165.84		162.23	160.31
27		172.03		168.17	166.32
28		178.24		174.20	172.28
29		184.35		180.18	178.24
30		190.65		186.27	184.10
31		196.70		192.59	190.15
32		202.85			196.06
33		208.87			201.94
34		215.00			208.55
35					214.70
36					221.84
37					227.48
38					234.99
39					241.29

TABLE VII

ROTATIONAL CONSTANTS

v	Lower state $^1\Pi_u$		Upper state $^1\Pi_g$	
	B_v''(cm.$^{-1}$)	$D_v''.10^6$ (cm.$^{-1}$)	B_v'(cm.$^{-1}$)	$D_v'.10^6$ (cm.$^{-1}$)
0	1.6084	6.6	1.7734	7.1
1	1.5912	6.5	1.7490	8.0
2	1.5738	6.4	1.7186	9.1
3	1.5564	6.9	1.6784*	(12)
4	1.5400	7.2	1.6175	17
5	1.5223	6.7	1.5227	25
6			1.4096	23
e	1.6170	6.3	1.7834	6.8
	$\alpha_e'' = 0.0172$ cm.$^{-1}$			
	$\beta_e'' = 0.13 \cdot 10^{-6}$ cm.$^{-1}$			

This value is somewhat less accurate than the others, since the 3–1 band from which it was obtained is badly overlapped. For the same reason the value of D_3' could not be determined independently but was taken from a reasonable interpolation of the other D values.
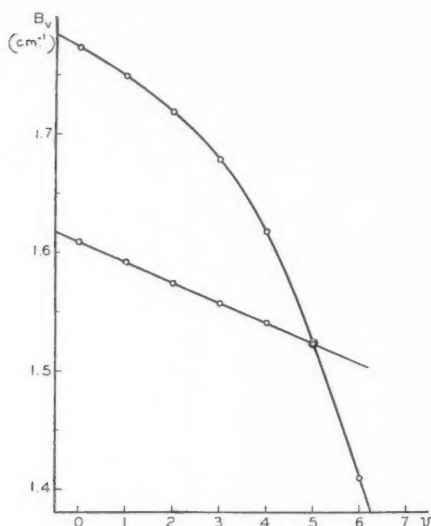
FIG. 1.

from B_e'' and B_e' using recent values for the atomic constants [see Herzberg (4)] are

$$r_e'' = 1.3182 \cdot 10^{-8} \quad \text{and} \quad r_e' = 1.2552 \cdot 10^{-8} \text{ cm.}$$

Some further bands found by Fox and Herzberg (2) were suspected by them to be tail bands of the Swan bands of C_2. Their fine structure is now being investigated in this laboratory.

Acknowledgments

References

1. DIEKE, G. H. and LOCHTE-HOLTGREVEN, W.   Z. Physik, 62 : 767-794.   1930.

2. FOX, J. G. and HERZBERG, G.   Phys. Rev. 52 : 638-643.   1937.

3. HERZBERG, G.   Astrophys. J. 89 : 290-292.   1939.

4. HERZBERG, G.   Molecular spectra and molecular structure I.   Prentice-Hall, Inc., New York.   1939.

5. JOHNSON, R. C.   Nature, 125 : 89-90.   1930.

6. KOPFERMANN, H. and SCHWEITZER, H.   Z. Physik, 61 : 87-94.   1930.

7. MULLIKEN, R. S.   Rev. Modern Phys. 4 : 1-86.   1932.

THE ALKALOIDS OF FUMARIACEOUS PLANTS

XXVI. *CORYDALIS CLAVICULATA* (L.) DC.[1]

BY RICHARD H. F. MANSKE[2]

Abstract

Corydalis claviculata (L.) DC. was found to contain protopine, partly racemized *l*-stylopine and cularine, together with a phenolic base or mixture of bases, *alkaloid F52*, which on methylation yields cularine. Attention is drawn to the fact that the alkaloid constituents do not point to as close a relationship with *C. lutea* and *C. ochroleuca* as suggested by taxonomists.

The writer has placed on record a chemical examination of *Corydalis lutea* (3) and of *C. ochroleuca* (4). It was pointed out that these two plants are regarded by botanists as being closely related, but the alkaloid constituents indicate that such is not necessarily the case. *Corydalis claviculata* (L.) DC. is also included in the same section (Stylotome), but the chemical examination, which forms the subject of the present paper, indicates that on this basis the relation can only be remote.

Protopine was readily isolated, but its occurrence in any particular plant of the Papaveraceae Family is of no value as a criterion of interrelations. Stylopine was found in small amounts, and its presence may indicate a distant relation to these plants which are rich in the protoberberine bases. Nevertheless, the fact that cularine (2) is the main constituent cannot be regarded as fortuitous and must be ascribed to a deep-seated mutation which may also have resulted in the scandent habit of the plant, a habit almost unique in the genus. It remains to be determined whether this is the only occurrence of cularine in the genus. Darwin (1) in his treatise on climbing plants has pointed out that *C. claviculata* presents a type intermediate between the two extreme types of climbers. The earliest types employ the leaves as clasping organs, while the more advanced types have well developed tendrils. The former type is represented in the Papaveraceae by the genus Fumaria and the latter is represented by Dactylicapnos, one species of which is now under investigation.

A basic fraction containing one or more phenolic alkaloids was also obtained. It has not been possible to obtain a base or a salt in a crystalline condition from this fraction, which on methylation with diazomethane gave an almost quantitative yield of cularine. It must therefore consist substantially of one or

more O-desmethylcularines. One such alkaloid is cularidine (2), and it was anticipated that it might be present, but it was not possible to isolate it from the phenolic material, which for convenience of reference will be designated *alkaloid F52.*

Experimental

The material for this investigation was collected in Holland near Ede. The collecting and drying were supervised by Dr. Jan Kalff, to whom the author expresses his great indebtedness. At the time of collection some seed had ripened, but for the most part the plants were in the flowering stage. There was available a total of 20.2 kg. of dried material, of which the roots constituted only an insignificant portion.

The standard procedure used by the author in previous investigations was applied successfully to this plant, although the phenolic base or bases did not have properties distinctive enough to be concentrated in any particular fraction.

Protopine

The isolation of pure protopine from fraction (BS) in this case was best accomplished by recrystallization as the hydrobromide. The regenerated alkaloid was then obtained in colourless crystals which melted at 211° C.* The total yield was 0.16%. No further bases were found in the mother liquors.

Stylopine and Cularine

The fraction (BC) as well as (EC), which proved to be almost entirely non-phenolic, was redissolved in hot dilute hydrochloric acid and the filtered solution allowed to remain for several weeks. During this time a sparingly soluble hydrochloride separated. It was recrystallized from hot water and the free base then regenerated by adding ammonia to a supercooled aqueous solution. The dried precipitate was recrystallized twice from chloroform-methanol, and then melted at 206° C. It proved to be identical with a specimen of partly racemic *l*-stylopine isolated from *C. lutea* (3) and on complete racemization it yielded *dl*-stylopine melting at 221° C. The yield was ca. 0.005%.

The filtrate from the stylopine hydrochloride was basified with ammonia and the liberated base extracted with ether. The ethereal solution was washed with water, dried over potassium carbonate, filtered with charcoal and evaporated to a thin syrup. Inoculation with a crystal of cularine induced immediate crystallization. The base thus obtained melted at 114 to 115° C. and when recrystallized from dry ether it melted sharply at 115° C. In admixture with a specimen of cularine from *Dicentra cucullaria* it melted at the same temperature.

The cularine remaining in the mother liquors was isolated as the sparingly soluble acid oxalate. (This salt melts at 245° C. with effervescence). The

* *All melting points are corrected.*

total yield of purified base was 0.25%.   The filtrate from the acid oxalate yielded a small amount of protopine only.

Cularine hydrochloride may be crystallized from hot water, in which it is readily soluble.   Better recovery of the salt is achieved if the base in hot methanol is neutralized with methanolic hydrogen chloride and then treated with ethyl acetate until the incipient turbidity just disappears on mixing. The crystals thus obtained are filtered off, washed first with methanol-ethyl acetate and then with the latter solvent.   The large, almost colourless, stout prisms melt at 207° C.

Alkaloid F52

The alkaloids represented by Fractions (BCE), (EEC), (BSE), and (EES) were purified separately, but in each case the procedure was that outlined below.

The dried residue was dissolved in cold dilute hydrochloric acid and the filtered solution (charcoal) diluted with much water and basified with ammonia. If the solution was not greatly diluted before basification the precipitated base coagulated to large masses which could not be conveniently dissolved in ether.   A large volume of ether was added and the mixture shaken until the insoluble suspended matter was uniformly distributed in the aqueous layer. The ether solution was then thoroughly washed with water and the solvent removed.   In this condition the products were colourless brittle resins.   In all cases the product was soluble in hot methanol, but separated as a gel on cooling.   Attempts to obtain crystalline bases from other solvents failed, as did attempts to obtain crystalline hydrochlorides or oxalates.   The base, or mixture of bases, thus obtained is referred to as alkaloid F52.   The yield was ca. 0.06%.

That the base or bases in these various fractions are closely related if not identical was demonstrated by methylating a small portion of each fraction. For this purpose a methanolic solution was treated with an excess of ethereal diazomethane and the resulting non-phenolic base converted into the acid oxalate.   The base regenerated from the latter salt in each case proved to be pure cularine (mp. and mixed mp.).

There was present in the combined mother liquors from which the acid oxalate had been filtered a very small amount of a non-phenolic base, which has not yet been obtained in a crystalline condition.

References

1. DARWIN, CHARLES.   Movements and habits of climbing plants, 2nd ed.   D. Appleton & Co., New York.   1901.
2. MANSKE, R. H. F.   Can. J. Research, B, 16 : 81-90.   1938.
3. MANSKE, R. H. F.   Can. J. Research, B, 17 : 89-94.   1939.
4. MANSKE, R. H. F.   Can. J. Research, B, 17 : 95-98.   1939.

THE ALKALOIDS OF FUMARIACEOUS PLANTS

XXVII. A NEW ALKALOID, *CHEILANTHIFOLINE*, AND ITS CONSTITUTION[1]

### By Richard H. F. Manske[2]

Abstract

Cheilanthifoline is the name now given to alkaloid F13. On methylation it has yielded sinactine and on ethylation it has yielded an O-ethyl ether (m.p. 144° C.), which on oxidation gave rise to 6-methoxy-7-ethoxy-1-keto- 1 : 2 : 3 : 4-tetrahydro-isoquinoline. Cheilanthifoline is therefore 2-O-desmethyl-sinactine. Further evidence has been adduced to show that alkaloid F36 is in fact a partly racemic sinactine.

The author has recorded the isolation of an alkaloid (F36) from *Fumaria officinalis* (6) which was recognized as isomeric and probably identical with the alkaloid sinactine, $C_{20}H_{21}O_4N$. Its low optical rotation indicated that it was a mixture of the laevo and the inactive forms. It has now been observed that oxidation with permanganate yields metahemipinic acid, and since it gives a positive test for the methylenedioxy group, formula (I), which is that of sinactine, is indicated.
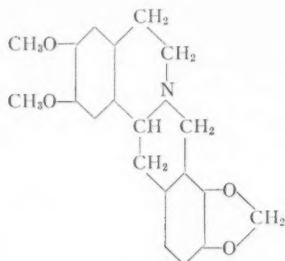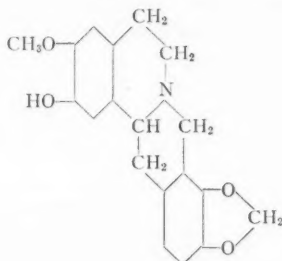
(I)   (II)

The oxidation product did not include 3 : 4- methylenedioxy-phthalic acid, which might have been anticipated. There are, however, a number of cases on record (1, 5) in which a benzene nucleus carrying a methylenedioxy group is destroyed by such oxidations, and this is only another example. It may be concluded therefore that the combined evidence is sufficient proof that alkaloid F36 is sinactine.

Further proof of this identity became available during a study of alkaloid F13 (6), which on methylation with diazo-methane yielded alkaloid F36. This alkaloid, for which the name *cheilanthifoline* is now proposed, has been

obtained in slightly larger relative quantities from *Corydalis cheilantheifolia*, and it has been possible to show that it is represented by formula (II). Ethylation with diazo-ethane yielded the corresponding O-ethyl ether melting at 144° C.*, which on oxidation with potassium permanganate gave rise to the corresponding corydaldine, 6-methoxy-7-ethoxy-1-keto- 1 : 2 : 3 : 4- tetra-hydro-isoquinoline. The latter was properly authenticated by means of specimens similarly prepared from the O-ethyl ethers of scoulerine and of isocorypalmine. In this case too the benzene nucleus carrying the methylene-dioxy group could not be obtained, further oxidation yielding only 4-methoxy-5-ethoxy-phthalic acid.

Experimental

Oxidation of Alkaloid F36 (Sinactine)

A solution of 0.2 gm. of the alkaloid in dilute hydrochloric acid was treated with an aqueous solution of sodium carbonate until the incipient turbidity was just permanent. An excess of an aqueous solution of potassium perman-ganate was added. After standing for two hours the mixture was decolorized with sulphur dioxide and evaporated to a small volume. It was then acidified with hydrochloric acid and extracted with ether. The residue from the extract was dissolved in water, treated with calcium acetate to precipitate the oxalic acid, and filtered. The filtrate was acidified with hydrochloric acid and again extracted with ether. The residue from the latter was heated on the steam bath to expel the acetic acid. It then crystallized with great facility. It was converted into the ethyl-imide by heating with an excess of alcoholic ethyl amine and evaporating to dryness. This product was sublimed in vacuo and after one recrystallization from hot methanol it melted at 232° C., either alone or in admixture with an authentic specimen of N-ethyl-metahemipinimide. The material in the mother liquor consisted of the same substance but slightly less pure. Redistillation of the more soluble fraction failed to show the presence of the 3 : 4- methylenedioxy-phthalic acid derivative.

Cheilanthifoline (Alkaloid F13)

The small amounts of this alkaloid available from *C. scouleri* (3) and from *C. sibirica* (4) were augmented by 0.1 gm. of the alkaloid from *C. cheilanthei-folia*, a plant now under investigation. The specimen from the last source melted at 184° C., and admixture with specimens from the other sources did not depress the melting point. Its high optical activity, $[\alpha]_D^{20}$ −311° ($c =$ 0.1100 in methanol), is indicative of considerable optical purity.

A small portion in methanol was methylated with diazo-methane. The non-phenolic base thus obtained melted at 177° C., and admixture with alka-loid F36 did not depress the melting point. The ethylation with diazo-ethane was carried out in methanol-ether. The non-phenolic base was purified by solution in dilute hydrochloric acid (sparingly soluble hydrochloride), basifi-cation with excess potassium hydroxide, and extraction with ether. The dried

* *All melting points are corrected.*

ethereal solution on evaporation to a small volume deposited colourless elong-
ated plates of cheilanthifoline O-ethyl ether which melt sharply at 144° C.
Calc. for $C_{21}H_{23}O_4N$: OMe + OEt as OMe, 17.59%. Found: OMe + OEt,
calculated as OMe, 17.67%.

Oxidation of Cheilanthifoline O-Ethyl Ether

A solution of this base (75 mg.) in 50 cc. of water containing a drop of
concentrated hydrochloric acid was treated with an aqueous solution of
sodium carbonate until a slight but permanent turbidity was produced. The
well-cooled mixture was then treated with an aqueous solution of potassium
permanganate (135 mg.). When the latter was used up the solution was
heated and filtered and the cooled filtrate extracted with ether (aqueous
solution A). The residue from the ether extract was dissolved in hot
water, the solution cooled, filtered, and again extracted with ether. The
residue from this extract was slowly sublimed in vacuo. The brilliantly
colourless crystals thus obtained melted sharply at 195° C. either alone or in
admixture with specimens of 6-methoxy-7-ethoxy-1-keto- 1 : 2 : 3 : 4- tetra-
hydro-isoquinoline similarly obtained from scoulerine (2, 3) and from isocory-
palmine (2).

The aqueous solution A from which the corydaldine was obtained was
heated to expel ether, cooled, and treated with potassium permanganate
until the colour remained permanent for one hour. The acidic product thus
produced was isolated as described under the oxidation of sinactine and
similarly converted into its ethyl imide. The distilled product melted at
195° C. and when recrystallized once from methanol it consisted of colourless
fine prisms melting at 205° C. either alone or in admixture with an authentic
specimen of N-ethyl-4-methoxy-5-ethoxy-phthalimide. N-ethyl- 3 : 4- methyl-
enedioxy-phthalimide could not be isolated from the more soluble fraction.

References

1. BARGER, G. and GIRARDET, A.   Helv. Chim. Acta, 14 : 481-504.   1931.
2. GADAMER, J., SPATH, E., and MOSETTIG, E.   Arch. Pharm. 265 : 675-684.   1927.
3. MANSKE, R. H. F.   Can. J. Research, B, 14 : 347-353.   1936.
4. MANSKE, R. H. F.   Can. J. Research, B, 14 : 354-359.   1936.
5. MANSKE, R. H. F.   Can. J. Research, B, 16 : 76-80.   1938.
6. MANSKE, R. H. F.   Can. J. Research, B, 16 : 438-444.   1938.

A STUDY OF THE COEXISTENCE OF THE LIQUID AND GASEOUS STATES OF AGGREGATION IN THE CRITICAL TEMPERATURE REGION. ETHANE[1]

By S. G. MASON[2], S. N. NALDRETT[3], AND O. MAASS[4]

Abstract

A careful study has been made of the position and nature of the meniscus and the distribution of opalescence in bombs containing ethane as the critical temperature is approached. Photographs of the phenomena have been made. The effect of shaking has been observed, and a type of shaking is described that is believed to hasten the attainment of equilibrium between the liquid and vapour phases. Using this type of stirring the coexistence curve of ethane has been determined. Relative temperature measurements are accurate to within $\pm 0.001°$ C.; absolute temperature measurements, to within $\pm 0.015°$ C. Density measurements are believed accurate to within 1 : 3000. The limiting curve has the classical parabolic shape up to $32.23°$ C., at which point the slope changes abruptly and the curve becomes flat along the density axis. The authors believe that at this temperature a dispersion of liquid and vapour occurs and that liquid still persists above this temperature. It is shown that the critical temperature as ordinarily determined in a stationary bomb cannot be accurately determined. The critical temperature can be determined precisely and without ambiguity when the bomb is shaken, and it is recommended that the value obtained in this way be used instead, as a physical measurement.

Introduction

In a recent review by the senior author (8) a large amount of evidence is described indicating that if a tube containing an appropriate amount of liquid is heated slightly above the temperature of disappearance of the visible meniscus, a physical heterogeneity can often persist. This discontinuity is not apparent to the naked eye, and attempts to photograph it by use of infra-red photographic plates led to the present investigation.

While the infra-red plates detected nothing more than did the eye, a number of strange effects were noticed that had not been observed before in this laboratory. For example, it was found that under certain conditions a visible heterogeneity could be destroyed by shaking the system, contrary to the results of Winkler and Maass's experiments on stirring (18). It was also observed that the characters of meniscus disappearance and opalescence formation were altered by shaking, and could be made reversible with respect to temperature. The experiments indicated strongly that a dispersion of one phase in the other occurs at the temperature of disappearance of the meniscus, and a survey of the literature revealed that a few similar observations have been made by a number of investigators, viz., Travers and Usher (15)

Altschul (1), Cardoso (2), and Schroer (14).   The concept of emulsification appears to have received scant attention from most investigators of the critical state, however, because of a purely qualitative experimental foundation and an entirely inadequate explanation of its mechanism.   Instead, the anomalies of the critical state have been explained by a "structural" difference between the liquid and gas (3, 8).

It is the aim of this and subsequent investigations to present new evidence of dispersion to show that the "dispersion" and "structure" hypotheses are not mutually exclusive, but rather can be combined to provide a more rational explanation of the critical temperature phenomena than any advanced heretofore.

Experimental

Preparation of Samples

In the preliminary stages of the investigation, the ethane was purified by fractionation in a Podbielniak distillation apparatus.   The temperature at which the meniscus disappeared in bombs containing ethane purified in this way showed considerable variation, which could be attributed only to the presence of impurities.   After this was realized, chemical purification was resorted to before distillation.   The ethane was passed through a train made up of a saturated water solution of bromine (sensitized by means of a tungsten lamp), potassium hydroxide solution, copper oxide at 300° C., and finally a trap immersed in dry-ice–acetone.   The gas was then distilled through a Podbielniak column.   Ethane purified in this manner gave consistent results.

Bombs of about 4 cc. capacity were made from Pyrex bomb tubing of 8 mm. i.d. and 3 mm. wall, with a 4 cm. length of capillary tubing on the open end.   These were sealed to the purification and storage system, and evacuated with baking.   The desired amount of ethane was then condensed into each bomb by means of liquid air, from a standard volume equipped with a manometer, and the bomb was sealed off.   The amount of gas condensed into the bomb, as determined in this manner, was used only as a guide to obtain approximately the desired filling, and was not used in the final calculation of the density of the system in the bomb.

Procedure

Two sample bombs were usually studied simultaneously by mounting them on a wheel, 4 in. in diameter, which was arranged vertically in a large well stirred thermostat bath equipped with windows and illuminated to permit close scrutiny.   The wheel could be rotated, and in the experiments in which the effect of shaking was studied, the speed adopted was about 30 r.p.m. The bath was regulated to within $\pm 0.001°$ C. and temperatures were measured with a Beckmann thermometer to a differential accuracy of $\pm 0.001°$ C. Absolute temperatures were measured to within $\pm 0.015°$ C.

Two main types of run were made, each involving a temperature sequence starting at 30° C., heating up through the critical temperature (32.2° C.) to various higher temperatures, and then cooling down to 30° C.   This was

done for certain bombs in a stationary position and for all bombs that were shaken.

In the "stationary" runs, times ranging from a minimum of 20 min. up to 15 hr. were allowed after the bath had come to thermal equilibrium. At each temperature in the sequence, the position and nature of the meniscus, and the distribution of opalescence, were observed.

In the "shaking" runs the time required for equilibrium was much less. It never exceeded two minutes, although 10 min. was usually allowed. Particular attention was paid to the temperature at which the meniscus disappeared or reappeared, at the top of the bomb, at the bottom, or within its confines. This was done for both increasing and decreasing temperature sequences.

The mean density of the system in each bomb was determined as follows. The bomb containing the ethane was suspended on a thread attached to one pan of an analytical balance and passing through the floor of the balance case, so that the bomb hung freely inside a steel pipe, to protect the observer from explosions. After weighing, the bomb was cooled in liquid air and the tip broken off, care being taken not to lose any fragments of glass. The empty bomb was weighed and the weight of ethane obtained by difference. The volume of the bomb was determined by finding the weight of mercury required to fill it. Density measurements are believed to be accurate to within 1 : 3000.

Results

The Behaviour of the Meniscus in Stationary Bombs

A number of bombs were examined in the stationary position and the phenomena of meniscus disappearance were observed. It was found that, in general, the results were substantially the same as those reported in the investigations of Travers and Usher (15), F. B. Young (19), and S. Young (20) on a wide range of substances such as ethyl ether, sulphur dioxide, pentane, hexane, and octane. A number of other effects, which might of course be specific for ethane, were observed in addition to those that these writers mention.

In order that the significance of these additional effects may be clearly understood, the behaviour of typical systems will be briefly described. It was found that, based on the behaviour of the systems, those examined fell into three categories depending upon the mean density of the filling.

Class 1. Below a density of 0.19 gm. per cc. the meniscus gradually fell as the temperature was raised, and disappeared at the bottom of the bomb before the critical temperature was reached.

Class 2. Between density limits of 0.19 and 0.23 the meniscus disappeared at the critical temperature within the confines of the bomb. The phenomena occurring in the systems in this class may be further subdivided as follows:

(a) The meniscus fell before it disappeared, and reappeared at the bottom of the bomb,

(b) The meniscus remained stationary on heating, and reappeared at the middle of the bomb,

(c) The meniscus rose on heating before it disappeared, and reappeared at the top of the bomb.

Class 3. Above a density of 0.23 the meniscus rose with increasing temperature and disappeared at the top of the bomb before the critical temperature was reached. The phenomena occurring in systems of Class 2 are of more interest than those in systems of the other two classes, and typical phenomena of each of the three subdivisions of this class will be described in greater detail.

The behaviour of the system in Bomb 19 (Table I) was typical of Class 2 *(b)*. On heating from 30° C. the meniscus remained in the middle of the bomb. Up to 32.20° C. the meniscus was sharp and flat, and no opalescence was noticeable except at the meniscus, which appeared brownish by transmitted light and looked like a thin white disc by reflected light. Above 32.20° C. the meniscus became less sharp, gradually broadening into a band of dense brown opalescence. The region of opalescence gradually expanded in both directions, and at 32.27° C. it could be detected throughout the bomb, while the maximum intensity where the meniscus had been, had greatly diminished. This continued until the temperature was 32.4° C. at which point no discontinuity could be detected by transmitted light, but by reflected light a region of greater opalescence could be seen in the middle of the bomb. On heating to 32.5° C., the opalescence disappeared and no heterogeneity could be detected either by reflected or transmitted light.

On cooling, the opalescence gradually appeared, uniformly distributed in the bomb, and as far as visual comparison would allow, at greater intensity than at the same temperature on heating. At 32.235° C. the contents of the

TABLE I

Bomb	Temp., °C.	Density, gm./cc.	Filling	Bomb	Temp., °C.	Density, gm./cc.	Filling
1	31.220	0.2606	L	18	32.230	0.2071	C
2	31.932	.2414	L	19	32.232	.2063	C
3	31.967	.2404	L	20	32.232	.2052	C
4	32.106	.2346	L	21	32.225	.2012	V
5	32.156	.2314	L	22	32.230	.2008	V
6	32.228	.2242	L	23	32.212	.2006	V
7	32.220	.2240	L	24	32.230	.2002	V
8	32.232	.2216	L	25	32.230	.1997	V
9	32.218	.2212	L	26	32.228	.1946	V
10	32.230	.2205	L	27	32.232	.1940	V
11	32.227	.2186	L	28	32.232	.1920	V
12	32.232	.2184	L	29	32.190	.1902	V
13	32.238	.2170	L	30	32.226	.1900	V
14	32.230	.2147	L	31	32.222	.1885	V
15	32.230	.2130	L	32	32.006	.1740	V
16	32.232	.2116	L	33	31.540	.1605	V
17	32.232	.2110	L				

bomb was intensely white by reflected light and reddish brown by transmitted light; on cooling to 32.232° a dense opalescent band appeared in the middle of the bomb. At 32.231° the opalescence suddenly seemed to coalesce to form the so called "wet fog" described by Young (19). This settled out rapidly to form a sharp meniscus in the middle of the bomb. The opalescence decreased at this point, although it could still be observed, now uniformly distributed throughout the bomb. As the temperature was lowered the opalescence decreased until it could no longer be seen at 32.0° C.

The behaviour of the system in Bomb 28 may be considered as typical of Class 2 *(a)*. The meniscus fell as the temperature was raised from 30° C., and at 31.8° C. it was sharp and flat, and the liquid occupied about one-third of the volume of the bomb. The meniscus fell with increasing rapidity on further heating, and above about 32.1° C. opalescence appeared and the meniscus began to broaden out as already described for Bomb 19. The indefinite character of the meniscus above this temperature made it impossible to detect whether the meniscus continued to drop until it reached the bottom of the bomb. However, the behaviour on cooling, and when the bomb was shaken, makes this seem probable. At 32.3° C. only a broad band of opalescence remained where a sharp meniscus was last seen. From this band, extending to the bottom of the bomb, presumably in the wake of the meniscus, the opalescence was more intense than in the upper part of the bomb. On further heating, the opalescence decreased and gradually became uniform until at about 32.4° C. no discontinuity could be detected.

In order that the first appearance of liquid on cooling could be easily detected, the observations were made with the bomb inverted so that the capillary was at the bottom. On cooling from above 32.4° C. the opalescence increased uniformly throughout the bomb. At 32.231° C. a "wet fog" appeared in the bomb from the point the meniscus had reached when it began to disperse, and extending to the bottom of the bomb. A meniscus appeared at the bottom of the bomb and rose rapidly as liquid phase settled out.

The phenomena of Class 2*(c)* are exemplified by the behaviour of the system in Bomb 8. At 32.0° C. the meniscus was sharp and there was no opalescence. At 32.2° the meniscus had begun to broaden out in the manner already described. The liquid occupied about three-fourths of the volume of the bomb at this temperature. At 32.30° only a dense band of opalescence marked the place where the sharp meniscus had been last seen. The opalescence from this band to the top of the bomb (in the wake of the meniscus?) was much more intense than in the lower part of the bomb. Further heating decreased the opalescence and at 32.35° C. the opalescence was uniform throughout the bomb and no discontinuity could be detected.

On cooling, only a slight uniform increase in opalescence occurred down to 32.231° C. At this temperature a "wet fog" appeared in the region of the bomb above the point at which the meniscus began to broaden, and a meniscus appeared at the top of the capillary.

Further mention will be made later of bombs in which the system showed the phenomena designated by Class 2(a) and Class 2(c).

The behaviour of the system in Bomb 32 was typical of that in bombs of Class I (vapour fillings). On heating, the meniscus fell steadily until the liquid phase disappeared at 32.10° C. The meniscus remained sharp throughout and only very slight opalescence was observable. On cooling, the meniscus reappeared at 32.006° C. at the very bottom of the bomb.

The behaviour of the system in Bomb 3 was typical of Class 3 (liquid fillings). On heating, the meniscus rose steadily, remaining sharp and clear, until the liquid filled the bomb at 32.10° C. On cooling, the first bubble of vapour appeared at 31.967° C. The opalescence was not appreciable throughout the observations.

For all observations of systems of Class 2, in which class the meniscus gradually broadened out as the temperature was raised, the exact temperature at which the optical discontinuity disappeared completely was ambiguous, and could not be reproduced satisfactorily, even by the same observer, better than within ±0.01° C. Moreover, it was found that in judging whether a discontinuity existed, a great deal depended upon the height and distance of the observer from the bomb. When the bomb was viewed from above or below, a discontinuity could often be seen that was not apparent in the horizontal direction. Within a distance of 10 in. from the bomb, discontinuities could be detected that could not be seen at greater distances. It was found, moreover, that the rate of heating had some influence upon the temperature of disappearance, rapid heating tending to raise it. In most of these runs the rate was about 0.02° per hour, in which case the meniscus disappeared about two-tenths of a degree above the temperature at which it reappeared on cooling.

The temperature of reappearance, whether at the top or bottom or within the bomb, was, on the contrary, well defined and could be reproduced within ±0.001° C. For example, in Bomb 19 the meniscus appeared in the centre, and the temperature was reproduced time and again to 32.232° C.

Young (19), Travers and Usher (15), and Maass and co-workers (6, 11, 18) do not mention any difficulty in determining the de la Tour temperature. Moreover, Young (19) reports that the temperature of disappearance for ethyl ether became identical with its temperature of reappearance on reducing the rate of heating below 0.1° C. per hour, a rate some five times as fast as the rate in the present experiments.

In comparing these effects it must be borne in mind that in the work of the other investigators mentioned above, the thermostatic control and measurement of temperature were at best within 0.01° C.; moreover the observers were at some distance from the bombs. It may easily be seen that, under these conditions, changes that are manifestly sharp over a single 0.01° C. interval when viewed at a distance, become far less so over 10 intervals of 0.001° C. in a bomb under close scrutiny.

Another interesting effect was observed with bombs that had been heated to the temperature at which no discontinuity could be detected (e.g., 32.5° C. in Bomb No. 19). If the bomb was suddenly inverted, a turbulence was noticed that was undoubtedly due to the intermingling of regions of different density and different refractive index; after inverting the bomb several times the effect disappeared. This, of course, corresponds to the heterogeneity persisting above the de la Tour temperature and already referred to in the introduction.

The Effect of Shaking

As for the samples examined in stationary bombs, it was found that the behaviour of the system in bombs examined in the experiments with shaking fell into three similar categories, defined by the mean density of the filling, although the density limits defining the categories were apparently different from those for stationary bombs.

Class 1. Below a density of 0.201_2 the meniscus disappeared at the bottom of the bomb below a critical temperature which we shall call T_s, namely, the temperature at which the meniscus disappears in a bomb of critical filling which is vigorously shaken.

Class 2. Between density limits of 0.205_2 and 0.207_1 the meniscus disappeared at T_s within the confines of the bomb.

Class 3. Above a density of 0.211_0 the meniscus disappeared at the top of the bomb below T_s.

For convenience these will be referred to as "vapour", "critical", and "liquid" fillings respectively. The density limits given here do not necessarily mark the precise limits of each class since the systems examined do not cover the entire density range without gaps in the continuity.

The phenomena occurring in systems of each class will again be described by considering a typical system of each class.

The behaviour of the system in Bomb 19 was typical of that of Class 2 (critical fillings). At 31° C., when the shaking was stopped, the liquid phase settled out immediately. There was no appreciable opalescence. As the temperature was raised, there was no considerable change in the behaviour of the contents of the bomb until T_s was approached. Above 32.1° C. there was a gradual increase in the opalescence, and the time required for the phases to separate, when shaking was stopped, increased. At all times the opalescence was evenly distributed as far as visual comparison would allow. At 32.19° C. the liquid had ceased settling after about 10 sec. At 32.230° C. about one minute was required. At 32.231° C. the contents of the bomb was intensely brown and turbid and immediately after shaking was stopped, wet clouds could be seen in turbulent motion. About two minutes was required for the phases to separate to form a sharp meniscus. At 32.232° C. the turbidity vanished, leaving a completely homogeneous, clear, light brown system, which remained unchanged after several hours at this temperature. The difference between the contents of the bomb at this temperature and at

0.001° C. lower was similar to that between a finely dispersed sol and one that has been partially coagulated. With further heating the brown colour gradually faded.

With cooling down the same effects occurred at precisely the same temperatures as on heating.

The limiting temperature T_s (32.232° C.) could be reproduced without ambiguity, both on heating and cooling, to within $\pm 0.001°$ C., the limit of accuracy of the Beckmann thermometer readings.

The photographs in Fig. 1, with the details given in Table II, demonstrate the behaviour of a representative critical filling. The bomb shown in these photographs is not listed in Table I, since it was prepared in the preliminary stages of this investigation, and contained some impurity, probably ethylene, to ensure the absence of which special precautions were taken in the case of the bombs listed in the table. The photographs were not repeated with a bomb containing a system of undoubted purity, because comparison of a pure system with the impure one showed that the phenomena associated with the disappearance of the meniscus were the same in both cases, the only difference being a shift in the temperature at which the effects occurred. The limiting temperature T_s for the system in the bomb shown was 31.944° C. compared to 32.232° C. for pure ethane.

TABLE II

Photograph	Temperature, °C.	Type	Remarks
i	31.850	Process	Meniscus sharp and concave; slight opalescence.
ii	31.900	Process	Meniscus sharp and less curved; greater opalescence.
iii	31.940	Process	Meniscus present (see vi) but process plate does not penetrate very intense opalescence.
iv	32.03	Process	No meniscus; opalescence considerably diminished.
v	32.09	Process	No meniscus; further decrease in opalescence.
vi	31.940	Infra-red	Meniscus sharp and flat; very intense opalescence.
vii	31.950	Infra-red	No meniscus after standing ¾ hour, opalescence slightly less intense than vi.

These photographs were taken in a sequence of increasing temperatures, but the same effects occurred at the same temperatures on cooling. It will be noticed that as the temperature was raised from 31.850° C. to 31.940° C. the meniscus flattened out but remained sharp and well defined and in the middle of the bomb. The opalescence also increased and became so intense at 31.940 that the process plate did not penetrate the reddish brown coloration (Fig. 1, iii), whereas the infra-red plate recorded a meniscus (vi) which
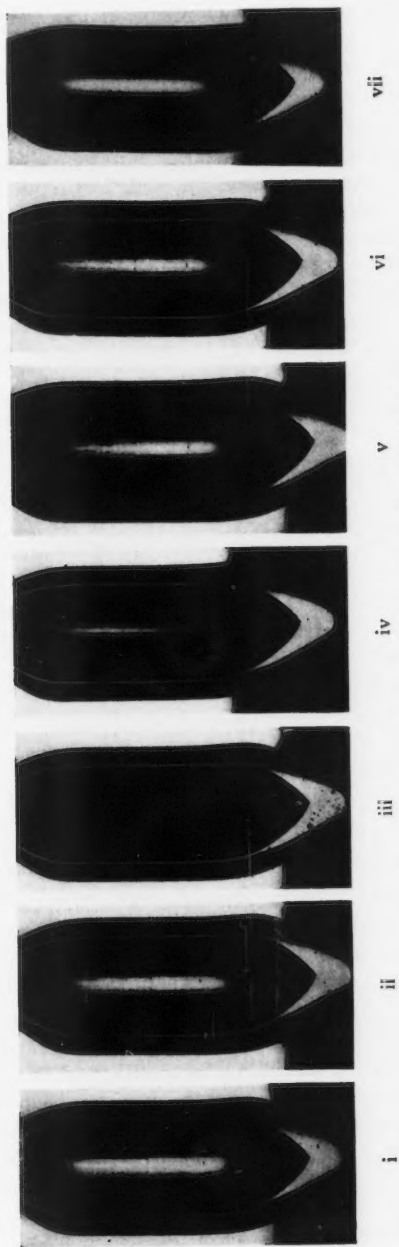
Fig. 1. *Photographs of the meniscus of ethane (shaking).*

was also visible to the naked eye.   At 31.950 no meniscus was present and the opalescence had decreased somewhat (vii).   On further heating the opalescence decreased rapidly, and the decrease was shown by process plates (iv and v).

The phenomena occurring in a system of Class 1 (vapour fillings) are shown in the case of Bomb 28.   As the temperature was raised the meniscus fell and the opalescence gradually increased and was uniformly distributed.   At 32.230° C. the liquid phase had diminished until only a tiny droplet remained. This could easily be seen, however, as it fell from top to bottom when the bomb was turned over.   At 32.231° C. the droplet had further decreased in size and at 32.232° C. no liquid phase was visible.   The opalescence was less than in critical fillings.   On cooling the first droplet of liquid appeared at 32.231° C.

The system in Bomb 8 was typical of systems of Class 3 (liquid fillings). As the temperature was raised the meniscus rose, and the opalescence gradually increased, uniformly distributed throughout the bomb.   At 32.231° C. a tiny bubble of vapour could be seen rising to the top as the bomb was turned over.   At 32.232° C. no vapour could be seen.   On cooling, the first trace of vapour appeared at 32.231° C.   In bombs containing systems of this class also, the opalescence was always less intense than in the case of critical fillings.

By shaking the contents of the bomb in the manner described in this investigation, the temperature at which the last droplet of liquid or the last bubble of vapour disappeared could be determined unambiguously and reproducibly, as closely as the temperature could be controlled.

Comparing the behaviour of the contents of Bomb 19 (critical filling) when shaken, with the behaviour when the bomb was in the stationary position, it is apparent that shaking has considerable influence upon the phenomena occurring between the critical temperature when shaken, T_s, and the de la Tour temperature.

    1. Shaking increases opalescence and distributes it uniformly.

    2. The visible discontinuity above T_s is destroyed and is succeeded by an apparently homogeneous system.

    3. The behaviour on shaking is reversible and identical with that on cooling a stationary bomb from above the de la Tour temperature.

The effect of shaking upon the meniscus behaviour is not restricted to temperatures above T_s, as can be seen from a comparison of the density limits that define the critical fillings as encountered in stationary and shaking experiments.   In the stationary runs the meniscus seemed to disappear within the confines of the bomb for systems of Class 2, having densities between 0.19 and 0.23.   Of this group, those systems in Class 2(a) (in which the meniscus fell before it disappeared and was found to reappear at the bottom of the bomb) when shaken are found definitely to be vapour fillings.   Those bombs that for stationary runs contained systems belonging to Class 2 (c) (in which

the meniscus rose before it disappeared and was found to reappear at the top) definitely fill with liquid on shaking. It is probable that these bombs actually fill when stationary, but the dispersion of liquid and vapour that forms at the meniscus as the temperature is raised, makes the line of demarcation of the phases so vague that it cannot be followed by the eye.

Further evidence of the effect of shaking below T_s was given by the following experiment. A bomb with critical filling (actually the bomb of which photographs are given) was slowly heated in the stationary position to a temperature $0.015°$ C. below its T_s, and the height of the meniscus above the bottom of the bomb was carefully measured with a cathetometer. The bomb was rotated for one minute and then carefully adjusted to its former position, and the height of the meniscus again measured. It was found that the meniscus fell from a height of 5.50_5 cm. to a height of 5.45_0 cm. above the bottom. No amount of shaking at the same temperature then moved it further. This was repeated six times and the same effect was observed.

The Coexistence Curve of Ethane

The temperatures of disappearance of the menisci of vapour, critical, and liquid fillings, together with their average densities, are tabulated in Table I and are plotted to sensitive density and temperature scales in Fig. 2.
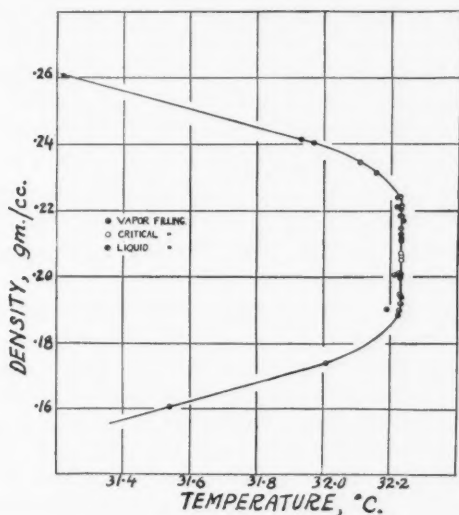

FIG. 2. *The coexistence curve of ethane.*

Three critical fillings are recorded in Table I (Bombs 18, 19, 20) with "shaking" critical temperatures that agree to within $\pm 0.001°$ C., the limit of accuracy of the temperature measurements. The "shaking" critical temperature of pure ethane may therefore be taken as $32.23_0 \pm 0\ 01_5°$ C.

Discussion

These observations may be adequately explained by assuming that, in the equilibrium state, there occurs a partial dispersion of vapour in liquid and liquid in vapour below T_s, becoming complete at and above T_s. A discussion of the mechanism and properties of such a system is reserved for a subsequent paper on the critical opalescence. By equilibrium state is here meant one reversible with respect to the parameter of temperature. It follows therefore that the systems observed on cooling in the stationary position from above the de la Tour temperature, and at all times with shaking, are equilibrium states; as already intimated, those observed on heating in the stationary position are largely transient.

It is assumed of course, that close contact between the two phases must precede their mutual dispersion, and this explains the intense opalescence in bombs that are shaken, as well as that of the expanding meniscus, if the critical opalescence is caused at least in part by dispersed droplets and not wholly by Einstein-Smoluchowski density fluctuations (4). Evidence for this will be presented in a subsequent report on the critical opalescence. In describing the behaviour of stationary runs, it was pointed out that in bombs containing systems of Class $2(a)$ and (c), the opalescence was more intense in the region through which the meniscus moved, than in the remainder of the bomb. Moreover, on cooling these bombs, a "wet fog" appeared, concentrated in these areas. These phenomena can easily be explained by assuming that a dispersion of liquid and vapour forms, when the phases are in contact. In this connection Travers and Usher (15) found that with sulphur dioxide the moving meniscus left a region of opalescence in its wake, but with ethyl ether the opalescence was most intense in front of the moving meniscus.

On cooling from above the de la Tour temperature, dispersed droplets appear uniformly throughout the system and undergo partial separation at T_s. The two phases that separate at T_s are not pure liquid and pure vapour but each contains the other dispersed in it.

In addition to the obvious mixing that occurs on shaking, there is another process that serves to explain the apparent discrepancy between these observations and those of Winkler and Maass (18). In their experiments it was found that gentle stirring that caused a visible interchange of the two phases did not affect the discontinuity in density above the de la Tour temperature. It must be remembered that in this region the density difference is small and the compressibility high. Violent shaking would therefore set up appreciable pressure gradients that would cause, on compression, liquid droplets to form in the vapour, and, on expansion, vapour bubbles in the liquid and so hasten the dispersion.

Much of this work has been justly criticized on the grounds that it is not susceptible to quantitative proof nor does it give tangible evidence of a two phase system above the de la Tour temperature. It was with the purpose of translating the qualitative observations to a quantitative basis that the

"shaking" coexistence curve of ethane was determined. If dispersion occurred on shaking, the density curve determined in this manner would lie entirely within that evaluated from PVT data using $\frac{\delta P}{\delta V} = 0$ as the criterion of a two phase system. It was planned that these measurements would be done in this laboratory, but experimental difficulties have prevented this to date.

Despite the lack of such data, there are a number of points of interest to the curve (Fig. 2), which resembles that of ethyl ether determined by Schroer (14). It will be noticed that below $32.23°$ C. (T_s), the envelope has the general parabolic form predicted by the classical theory and characteristic of that obtained from PVT data on most substances. At T_s, however, there is an abrupt change in shape, and the curve becomes approximately flat along the density axis. Three points in the centre of this portion represent critical fillings whose T_s agree within the experimental error of $\pm 0.001°$ C. From a comparison of the sudden formation of the meniscus in the critical fillings with its gradual reappearance in the liquid and vapour fillings, it is contended that the coexistence curve is mathematically flat across the range of critical fillings. This implies that T_s is always constant within the limit of error, no matter how small the latter is made.

According to the classical theory of Andrews-van der Waals, the critical phenomena should be observed only if the filling of the bomb conforms to a unique density given by the Cailletet-Mathias rule. It assumed that at the critical temperature there is a transition of the two phase system liquid-gas into a one phase system, the liquid phase ceasing to exist. This theory of continuity has been supported by Kuenen (7) and by Onnes (13), and has been summarized more recently by Jellinek (5, pp. 917-921). These investigators believe that the anomalies of the critical phenomena are due to the presence of impurities or of temperature gradients or to the absence of stirring. It has been shown in a recent review by the senior author (8) that the anomalies persist in investigations in which these possible sources of error have been avoided.

Moreover, in the present investigation, critical phenomena have been observed over a density range of 0.205_2 to 0.207_1, and it is probable that the precise limits of the range over which critical phenomena may be observed are somewhat wider than the limits examined in this investigation. Since the observations were made on bombs that were vigorously shaken, the claims that stirring corrects for the anomalies of the critical phenomena are untenable. A temperature gradient over the length of the bomb is very improbable in a bomb that is rotated in the manner described in this investigation. The regularity with which the individual observations trace out the coexistence curve is evidence for the purity of the ethane used in the investigation.

A better hypothesis is that of Traube (16): "the two phases liquid and gas co-exist above and below the critical temperature and we define the critical temperature as that temperature at which the two solubility curves intersect,

in which the liquid and the gas phases are mutually soluble in all ratios.   The liquid phase exists even above the critical temperature in a certain range of temperature.''   The evidence of this investigation is in agreement with this hypothesis, but the temperature at which liquid and gas become completely miscible is not the de la Tour temperature, which is usually meant by the term "critical temperature", but the temperature T_s .

In the following paper (12), similar studies for the system ethylene are described.   Of particular interest is the comparison of the two density curves, and for convenience this will be discussed at this point.   Both curves represent equilibrium values in the sense that they can be approached reversibly and correspond to ostensibly the same quantities independently determined.

As was predicted, the shaking curve lies entirely within the envelope of the PVT phase-density curve.   This is therefore unequivocal evidence of the existence of a stable two phase system above T_s , and is in agreement with the theoretical conclusions of Mayer and Harrison (9, 10).   The difference between the curves is not restricted to the region above T_s (9.21° C.) but also appears below as far as 8.9° C.   This confirms the observations made on the effect of shaking below T_s .

It is convenient now to discuss the term "critical temperature" in the light of its experimental determination.   According to the classical theory of van der Waals (17) the temperature of disappearance of the meniscus is identical with the temperature at which $\dfrac{\delta P}{\delta V} = 0$ and $\dfrac{\delta^2 P}{\delta V^2} = 0$.   A survey of the critical constants shows that this is not so, and that no great effort has been made to explain the discrepancy.   The reason for this difference is now apparent in the light of dispersion.

It has been shown that the de la Tour temperature cannot be accurately determined. T_s , on the other hand, can be determined to any degree of accuracy and without ambiguity.   It is therefore suggested that the de la Tour temperature be rejected as a useful physical quantity and replaced by T_s .   This would assign two characteristic critical temperatures, T_s , and T_c determined from PVT data, to each substance and give a measure of the discontinuity effect.

References

1. ALTSCHUL, M.   Z. physik. Chem. 11 : 577-597.   1893.
2. CARDOSO, E.   J. chim. phys. 10 : 470-496.   1912.
3. CLARK, A. L.   Chem. Rev. 23 : 1-15.   1938.
4. EINSTEIN, A.   Ann. Physik, 33 : 1275-1298.   1910.
5. JELLINEK, K.   Lehrbuch der physikalischen chemie.   Vol. 1.   F. Enke, Stuttgart.   1923.
6. GEDDES, A. L. and MAASS, O.   Trans. Roy. Soc. London, A, 236 : 303-332.   1937.
7. KUENEN, J. P.   Die Zustandsgleichung der Gase und Flüssigkeiten und die Kontinuitäts-
     theorie.   Vieweg und Sohn, Braunschweig.   1907.
8. MAASS, O.   Chem. Rev. 23 : 17-28.   1938.

9. MAYER, J. E. and HARRISON, S. F. J. Chem. Phys. 6 : 87-100. 1938.

10. MAYER, J. E. and HARRISON, S. F. J. Chem. Phys. 6 : 101-104. 1938.

11. McINTOSH, R. L. and MAASS, O. Can. J. Research, B, 16 : 289-302. 1938.

12. NALDRETT, S. N. and MAASS, O. Can. J. Research, B, 18 : 118-121. 1940.

13. ONNES, H. K. and FABIUS, G. H. Univ. Leiden. Proc. Acad. Amsterdam, 10 : 215-230. 1909.

14. SCHROER, E. Z. physik. Chem. 140 : 241-253. 1929.

15. TRAVERS, M. W. and USHER, F. L. Proc. Roy. Soc. London, A, 78 : 247-261. 1906.

16. TRAUBE, I. Trans. Faraday Soc. 34 : 1234-1235. 1938.

17. WAALS, J. D. VAN DER. Kontinuität der gasförmigen und flüssigen Zustandes. Leipzig. 1881.

18. WINKLER, C. and MAASS, O. Can. J. Research, 9 : 65-79. 1933.

19. YOUNG, F. B. Phil. Mag. 20 : 793-828. 1910.

20. YOUNG, S. Z. physik. Chem. 70 : 620-626. 1910.

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A STUDY OF THE COEXISTENCE OF THE LIQUID AND GASEOUS STATES OF AGGREGATION IN THE CRITICAL TEMPERATURE REGION. ETHYLENE[1]

By S. N. Naldrett[2] and O. Maass[3]

Abstract

The coexistence curve of ethylene has been determined in a manner similar to that described in a previous investigation on ethane (9). It is found to lie entirely within the coexistence curve determined by *P-V-T* methods by other investigators (6). This is considered to be evidence for the formation of a dispersion of liquid and vapour before the critical temperature is reached. The term "critical dispersion temperature" is suggested for the temperature at the apex of the coexistence curve determined by the disappearance of the meniscus in a bomb shaken in the manner described in this investigation. The apex of the curve determined by *P-V-T* methods is the true critical temperature, beyond which liquid is not stable. The classical critical temperature, determined by the disappearance of the meniscus in a stationary bomb, is an indefinite point between these two.

Introduction

In a previous investigation (9) the authors determined the coexistence curve of ethane. A type of shaking was devised which decreases the time necessary for the liquid and vapour phases to come to equilibrium, and which enables the observer to measure the temperature of disappearance of the meniscus precisely and without ambiguity. The coexistence curve for ethane was found to have the classical parabolic form up to 32.23° C., at which point the curve becomes flat along the density axis. It was suggested that the liquid and vapour phases become completely miscible at this temperature.

The present investigation describes the coexistence curve for ethylene determined in the same manner. The coexistence curve for this system has also been determined by *P-V-T* methods by other investigators, and a comparison of the two is presented. It is considered that the data presented constitute conclusive evidence of the formation of a dispersion of liquid and vapour.

Experimental

The experimental technique was precisely the same as already reported for the investigation on ethane (9) except that no chemical method of purification was necessary for ethylene. One Podbielniak distillation consistently gave a pure product.

For experiments made using a stationary bomb a method of mounting was so designed that the bomb would be rigid. The bomb was wired on to a copper rod, the lower end of which was soldered on to the bottom of the thermostat bath, and the other end securely clamped to a framework independent of the thermostat assembly.

Results

The behaviour of ethylene was found to be essentially the same as that reported for ethane.

The coexistence curve was determined in the manner described for ethane (9). The data are presented in Table I and are shown plotted in Fig. 1. The limiting curve determined independently by Dacey, McIntosh, and Maass (6) by *P-V-T* methods is also plotted in Fig. 1 for comparison; it will be discussed later.

TABLE I

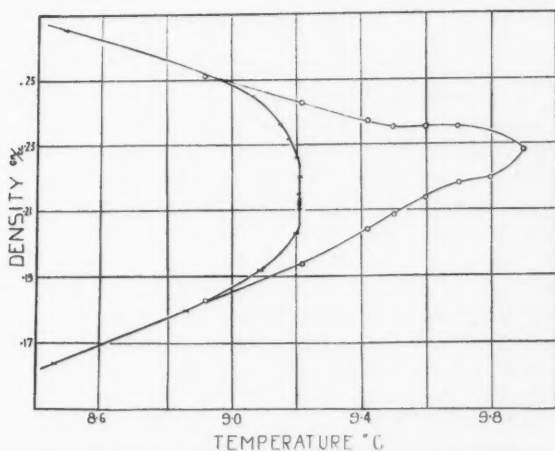| Bomb	Temperature, °C.	Density, gm./cc.	Filling	Bomb	Temperature, °C.	Density, gm./cc.	Filling
1	9.206	0.2102	C	10	9.150	0.2360	L
2	9.210	.2114	C	11	9.068	.2447	L
3	9.207	.2120	C	12	8.792	.2562	L
4	9.206	.2124	C	13	8.484	.2647	L
5	9.210	.2137	C	14	8.461	.1639	V
6	9.204	.2153	C	15	8.856	.1797	V
7	9.208	.2202	L	16	9.092	.1916	V
8	9.198	.2260	L	17	9.194	.2028	V
9	9.172	.2316	L				

FIG. 1. *The coexistence curve of liquid and vapour ethylene.* x, *Coexistence curve of ethylene in a shaken bomb.* o, *Coexistence curve determined by P-V-T methods.*

The critical temperature on shaking is found to be 9.21° C. ± 0.015° C. The temperature of disappearance of the meniscus determined in the usual manner in a stationary bomb was found to be not precisely definable. The meniscus in this case does not disappear sharply but gradually fades out as the temperature is raised. Therefore, the temperature at which apparent homogeneity is reached may be expected to depend upon the observer, and

upon the method of observation. The size of the bomb and the rate of heating also affect the temperature at which the meniscus disappears. For the bombs used in this investigation, observed directly from a distance of about one foot, this temperature was repeatedly found to be $9.3_6°$ C. For a much larger bomb used by Dacey, McIntosh, and Maass in their investigation, and observed from a distance of five feet by means of a telescope, the meniscus disappeared consistently at $9.5_0°$ C. The critical temperature on shaking, on the contrary, could be measured precisely to $0.001°$ C., and this limit depended only upon the accuracy of temperature control.

It was considered important to discover whether the meniscus would disappear at the same temperature in a stationary bomb as in a shaken bomb, if sufficient time were allowed. For this purpose, Bomb 2, containing a critical density, was rigidly supported in the bath, and thermostated for a long period at a temperature only $0.005°$ C. above the temperature at which the meniscus disappeared when the bomb was shaken. At the end of eight hours no meniscus was visible, but on disturbing the bomb a turbulence was observed, indicating two regions of different refractive indices. When the bomb was left for 24 hr. before being disturbed, no turbulence could be detected. Apparently the contents of the bomb was completely homogeneous. This experiment was repeated several times with the same result.

Discussion

The shape of the coexistence curve is similar to that found for ethane. Below $9.21°$ C., the critical temperature of ethylene in a shaken bomb, the curve has the classical parabolic shape. At this point, however, there is an abrupt change in slope, the curve becoming flat along the density axis. It will be observed that the coexistence curve determined in the manner described by the authors lies entirely within that determined by P-V-T methods by Dacey, McIntosh, and Maass. The obvious explanation of this is that a dispersion of liquid and vapour forms, so that the apparently one-phase system present in the bomb at the temperature at which the meniscus disappears is not pure liquid nor pure vapour, but a dispersion. The densities measured therefore do not lie on the curve obtained by P-V-T methods, but somewhere inside. At the temperature at which the curve becomes flat along the density axis, liquid and vapour become completely miscible, although both phases still exist above this temperature. For this reason the term "critical dispersion temperature" may be applied to this temperature, to distinguish it from the true critical temperature which will be discussed later.

The area enclosed by the crosses represents the area in which there can exist systems that are heterogeneous to the eye. The area enclosed by the circles represents the area in which a heterogeneous system of liquid and vapour exists as determined by P-V-T measurements. The apex of the latter curve is the true critical temperature, beyond which liquid is no longer stable. That is, liquid persists up to this temperature although the meniscus has disappeared. The authors consider that in the area between the "critical

dispersion temperature" and the true critical temperature there exists what may be described as a "macroscopically homogeneous" but "microscopically heterogeneous" system.   Both liquid and vapour are present, but the liquid is dispersed in droplets of submicroscopic dimensions, but of sufficient size to cause opalescence.

It has been suggested in the literature from time to time that a dispersion forms at the critical temperature, more especially as an explanation for the critical opalescence (1–5, 7, 8, 10–12).   Up to the present, however, no conclusive quantitative evidence has been given to support the hypothesis.

Although the "critical dispersion temperature" is the temperature at which the meniscus disappears in a bomb that is vigorously shaken, it may be repeated here that the meniscus disappears at the same temperature in a stationary bomb provided that sufficient time is allowed for equilibrium.   Apparently the pressure fluctuations that accompany violent shaking are not essential to produce homogeneity.   The effect of shaking in decreasing the long time lag found for a stationary bomb is obviously that it hastens the dispersion of one phase in the other by intermixing.   Moreover, it has been observed that shaking increases the opalescence; this might be expected if it resulted from a dispersion of one phase in the other.

The authors suggest that the critical temperature as defined by the disappearance of the meniscus in a stationary bomb be abandoned as a physical measurement, since it is neither the true critical temperature nor the "critical dispersion temperature", but is some indefinite point between them.   The "critical dispersion temperature", which is the same as the temperature of reappearance of the meniscus on cooling, can be precisely determined and would be more valuable as a physical measurement.   However, it should not be confused with the true critical temperature, at which liquid ceases to be stable, and which cannot be determined by a direct visual method.

References

1. ALTSCHUL, M.   Z. physik. Chem. 11 : 577-597.   1893.
2. BOOTH, H. S. and SWINEHART, C. F.   J. Am. Chem. Soc. 57 : 1337-1342.   1935.
3. BRADLEY, W. P., BROWNE, A. W., and HALE, C. F.   Phys. Rev. 26 : 470-482.   1908.
4. BRADLEY, W. P., BROWNE, A. W., and HALE, C. F.   Phys. Rev. 27 : 90-106.   1908.
5. CARDOSO, E.   J. Chem. Phys. 10 : 470-496.   1912.
6. DACEY, J. R., McIntosh, R. L., and MAASS, O.   Can. J. Research, B, 17 : 241-250.   1939.
7. DONNAN, F. G.   Chem. News, 90 : 139.   1904.
8. DONNAN, F. G.   Z. physik. Chem. 46 : 197-212.   1904.
9. MASON, S. G., NALDRETT, S. N., and MAASS, O.   Can. J. Research, B, 17 : 103-117. 1940.
10. OSTWALD, WOLFGANG.   Kolloid-Z. 64 : 50-62.   1933.
11. SHAPOSHNIKOV, K.   J. Russ. Phys.-Chem. Soc., Phys. Part 56 : 581-592.   1924.
12. TRAUBE, I.   Kolloid-Z. 70 : 302-305.   1935.
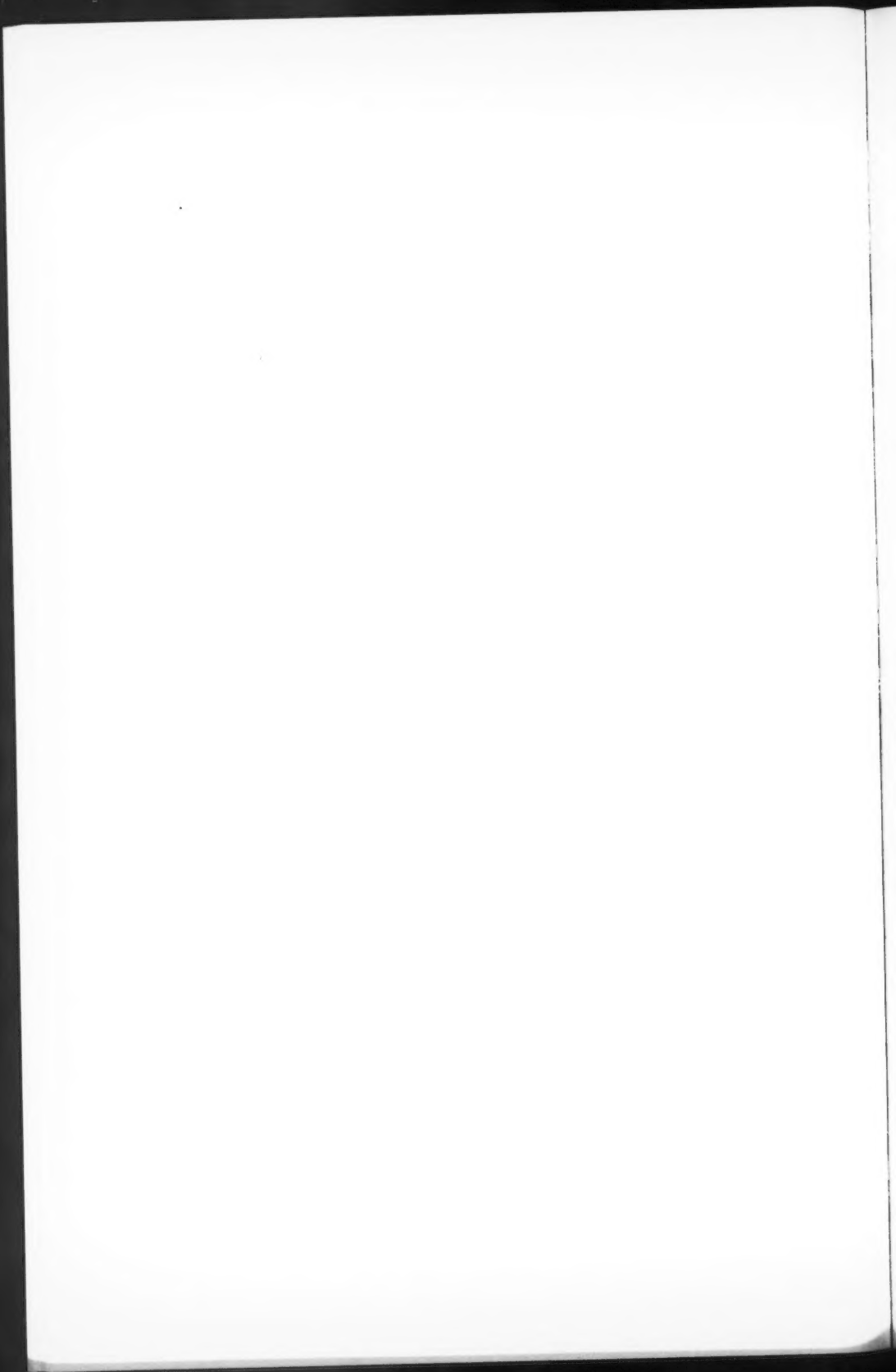
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